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BOSTON UNIVERSITY
GRADUATE SCHOOL

Thesis

POLAROGRAPHIC BEHAVIOR AND LIGHT ABSORPTION OF CERTAIN NICKEL CHELATES

by
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(B.S., Bates College, 1943)
submitted in partial fulfilment of the
requirements for the degree of
Master of Arts
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Chapter I

THE PROBLEM AND ITS TREATMENT

The principal purpose of this study was the investigation of the stability and structure of certain chelated nickel compounds. Previous investigators, whose work will be mentioned in detail later, have found that the coordination complexes of nickelous ion possess an interesting variation between square planar and tetrahedral configurations that is accompanied by a marked change in such physical properties as magnetic susceptibility, light absorption, and solubility.

Two different approaches to the problem have been made. An initial survey of the polarographic behavior of the nickel chelates was conducted to determine the relative stability and structure of the several members of a given series. Also, in a further attempt to gain additional information as to the structure of these compounds, their absorption spectra in the visible region have been determined in two types of solvent.

I. THE PROBLEM

A series of nickel chelates formed from nickel disalicylaldehyde and nickel di-(3-ethoxysalicylaldehyde) were investigated.

In using the polarographic technique, it is necessary to have a suitable supporting electrolyte. After this was found, the polarograms of the various members of the series were determined. These current-voltage curves were then analyzed to arrange the compounds in order of their relative stability.

The absorption spectra of the nickel di(3-ethoxysalicylaldehyde) series were determined in the visible region using both benzene and pyridine as solvents. The correlation between these extinction curves and their magnetic susceptibility was then studied.

II. ORGANIZATION OF THE THESIS

In the remainder of the thesis, the following scheme of presentation is used. First, a brief survey of the work done by previous investigators on the structure of the coordination complexes of nickel is presented. Attention is then given to the work done on certain copper chelates using the polarograph to determine stability followed by a discussion of the polarographic reduction of the simple nickel ion.

The third chapter is devoted to a description of the experimental work carried out using the dropping mercury electrode, and presentation of the polarograms obtained. Such generalizations as are justified are advanced at this point.

The experimental technique used in determining the absorption spectra of the nickel di-(3-ethoxysalicylaldehyde) series is discussed in the fourth chapter.

A summary of the conclusions reached as to the structure of the coordination complexes of nickel is made in the fifth chapter.

The appendix contains the spectrophotometric data from which the extinction curves were plotted.

CHAPTER II

REVIEW OF THE LITERATURE

In his discussion of the inner complexes of nickel ion, Pauling states:

> factors which determine whether the diamagnetic square or the paramagnetic tetrahedral configuration will be assumed by a nickel complex cannot be stated precisely. (1)

He further states that there is good evidence for correlation between the color of a complex and its bond and coordination type. While it is true that in general the paramagnetic complexes are green or blue in color and that the diamagnetic complexes are bright red, through reddish brown to yellow, too many exceptions are found to use this as a criterion of bond type.

Polarographic Technique No previous work has been done on the polarographic reduction of the chelate compounds formed with nickel ion. There is also little to be found concerning the use of the polarograph with respect to other metals forming inner complexes of this type. Lingane (2) discusses the polarographic reduction of metal ammines, cyanides, oxalates, in aqueous solution in a review paper. Of special interest in the present study is the work done by Calvin and Bailes (3) on cupric ion complexes of salicylaldehyde and its derivatives. These investigators showed that using as

a solvent 50% by volume aqueous pyridine some of the copper complexes dissociated to give a cupric-pyridine ion and the chelating group. A comparison of the apparent half-wave potentials indicates that the most important structural consideration affecting the stability of the copper chelates is the tying together of the two halves of the chelate molecule about the cupric ion.

As a basis for the present investigation the earlier findings on the polarographic reduction of the nickel ion in various solvents are of importance. Lingane (4) reports that in non-complex forming electrolytes the nickel hexaquo ion is reduced irreversibly at - 1.1 v. vs. the saturated calomel electrode. The diffusion current is well-defined and proportional directly to the concentration of nickelous ion when gelatin or methyl red in slightly acid solutions is added to suppress the maximum.

When a complex forming substance is added to an aqueous solution of nickelous ion, the half-wave potential is found to be shifted to a more positive value. Thus, in a solvent which is 1 N in potassium chloride and 0.5 M in pyridine nickel is reduced at - 0.78 v. vs. the saturated calomel electrode. (5).

The necessity of suppressing the maximum of nickel is apparent since any peak distorts the true shape of the polarographic curve. The literature mentions the use of several suppressors that work well in aqueous solutions; these are methyl red in acid solution, basic fuchsine, gelatin,

and thymol blue. (6) No mention is made of the behavior of these same suppressors in solutions containing high percentages of organic solvents.

Light Absorption. A number of investigators have used the absorption of light in the visible and ultraviolet regions to study the various inner complexes of nickel in attempts to determine the factors influencing their structure.

The work of French, Magee, and Sheffield on several organic coordination compounds of nickel showed that for nickel disalicylaldehyde and nickel di-(salicylal)-propylenediimine the substitution of two nitrogen atoms for two oxygen atoms caused;

> (1) an increase in the number of absorption maxima. (2) moved the ultra-violet maximum to longer wave-lengths, and (3) moved the visible maximum to shorter wave-lengths. The last two effects result in the long wave-length bands approaching each other so closely that one may become merely a step-out in the nitrogen containing complex. [plotted absorption band]. (7)

It is to be noted that in this same work bis-formyl camphor ethylene diamine in methyl alcohol solution was found to exist in both paramagnetic and diamagnetic forms. The equilibrium ratio was determined as approximately one-third of the former to two-thirds of the latter. The effect of the solvent was postulated as causing the shift in configuration. This observation was later confirmed by Willis and Mellor. (8)

Willis and Mellor studied the magnetic moments of internal nickel complexes in solution and found that a number which are diamagnetic in the solid state are paramagnetic in solution. (8)

They advanced the theory that the compounds exhibited a magnetic moment of 3.2 B.M. (the value for two unpaired spins) in pyridine have formed an octahedral complex using two pyridine molecules. For the cases where the moment is between 0 and 3.2 B.M. in solvents other than pyridine, they propose that the observed paramagnetism is due to a proportion of the chelate molecules being converted by the effect of the solvent from a square planar configuration to a tetrahedral form having two unpaired electrons. The formation of an octahedral complex is said to be out of the question in non-pyridine solutions. The alternative theory that the magnetic moment is due to the dissociation of the complex into nickel ions and chelate molecules is discarded because of certain evidence obtained from conductivity measurements and reaction rates that indicates that the magnitude of the dissociation is too small to produce the moments observed.

In a study of light absorption of nickel complexes in alcohol McKenzie et al (9) found that in paramagnetic complexes the nickel atom makes very little contribution to the absorption spectrum. The diamagnetic complexes, however, are characterized by the appearance of a broad band of considerable intensity in the region of 410 millimicrons which is

attributed to the presence of the nickel atom. The investigators noted that in the case of the paramagnetic complexes a weak nickel band occurs similar to that found for simple nickel salts which are also paramagnetic.

A. V. Kiss, P. Csokan, and G. Nyiri (10) measured the absorption spectra of di(salicylal)-ethylenediimine complexes having different metal atoms as the central atom. They determined that the absorption of the di-(salicylal)-ethylenediimine molecules is due to the excitation of the π electrons of the azomethine group $\doteq C=N-$ and the benzene nucleus. The band in the visible is said to be due to the hydrogen bridge formed using the unshared pair of the nitrogen atom.

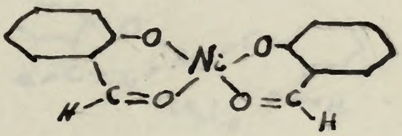
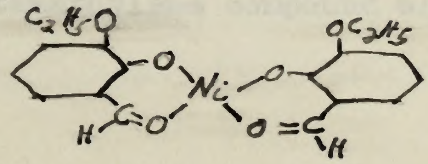
CHAPTER III

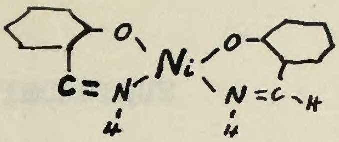
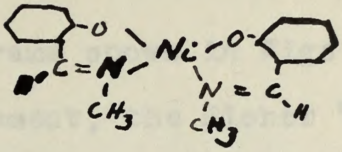
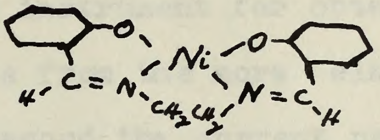
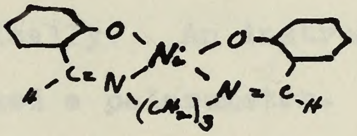
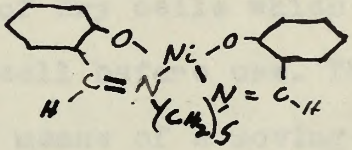
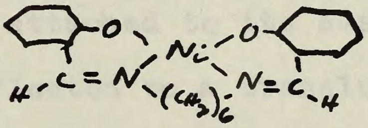
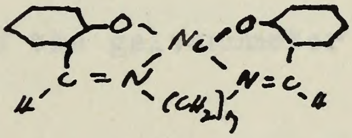
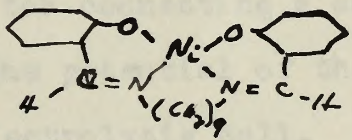
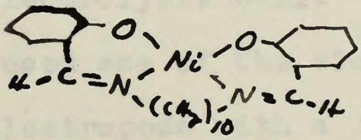
POLAROGRAPHIC BEHAVIOR OF NICKEL CHELATES

The nickel chelates under investigation were formed by the intramolecular coordination of a bivalent nickel atom, which has orbitals available in the outer valence shell, and salicylaldehyde or its derivative, 3-ethoxysalicylaldehyde, which have an unshared pair available on each oxygen atom. In the complex, the carbonyl oxygens still retain certain properties characteristic of aldehydes in that they are able to react with ammonia to form compounds of the type exemplified by nickel disalicylaldimine (III). They also react with amines to form imines as in IV and V.

The samples used were previously prepared and analyzed by Dr. R. H. Bailes. The two series were made using nickel disalicylaldehyde and nickel di(3-ethoxysalicylaldehyde) as parent compounds.

The compounds used are listed for future reference together with their magnetic susceptibility.

Name	Formula	Magnetic Susceptibility
I nickel disalicylaldehyde		paramagnetic green
II nickel di-(3-ethoxysalicylaldehyde)		paramagnetic yellow

III nickel di-(salicylald-imine)		diamagnetic red
IV nickel di-(salicylal-methylimine)		diamagnetic green
V nickel di-(salicylal)-ethylenediimine		diamagnetic red
VI nickel di-(salicylal)-trimethylenediimine		diamagnetic yellow
as dihydrate		paramagnetic green
VII nickel di-(salicylal)-pentamethylenediimine		diamagnetic red-brown
VIII nickel di-(salicylal)-hexamethylenediimine		diamagnetic dark green
IX nickel di-(salicylal)-heptamethylenediimine		diamagnetic yellow green
X nickel di-(salicylal)-nonamethylenediimine		diamagnetic yellow
XI nickel di-(salicylal) decamethylenediimine		diamagnetic green

The ethoxy substituted compounds are the same in color with the exception of the heptamethylene compound which is brown.

I. EXPERIMENTAL TECHNIQUE

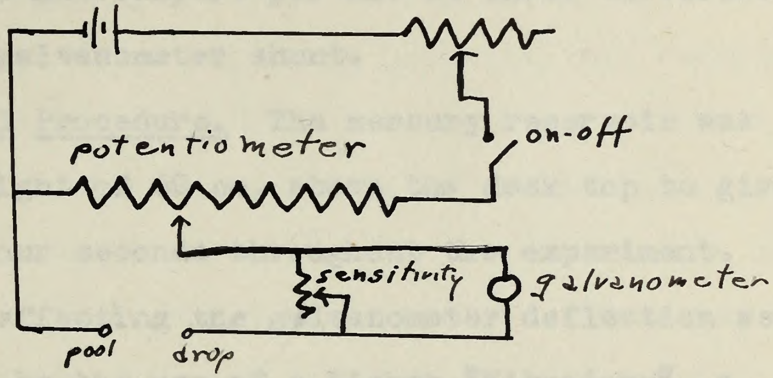
Apparatus. The polarograms shown in Figs 1-19 were made with a commercial instrument, the Fisher "Elecdropode". This is a manually operated instrument for obtaining current-voltage curves which differs from the more elaborate polarograph in that it does not record the current produced by a change in potential automatically. An instrument of this type is more accurately termed a polarometer.

The operating potential for the dropping mercury electrode is supplied by a set of dry cells which are calibrated against an Eppley standard cell before use. The current through the cell is read by means of a moving-coil type galvanometer that has a mirror attached to its suspension. The light from the mirror is reflected to a translucent scale calibrated in millimeters. A galvanometer shunt is used to adjust the sensitivity of the galvanometer over a considerable range.

Provision is also made for connecting a saturated calomel electrode to determine the potential of the mercury pool used as the anode of the electrolysis cell.

The electrolysis cell used was of the simple open type furnished with the Fisher-Electropode with a lead fastened to the bottom to make contact with the mercury anode pool. The electrolysis cell clamps to the outside of the case.

With the exception of the electrode assembly, all parts of the equipment are enclosed in a single housing. The circuit diagram below shows the essential features of the instrument.



Galvanometer Calibration. The Fisher "Elecdropode" measures current only in arbitrary units of galvanometer deflection. For a theoretical study of the type undertaken here, it was deemed advisable to calibrate the instrument in microamperes so that measurements made with other instruments would be comparable.

The method of calibration used was that described by Kolthoff and Lingane. (11) A precision resistance box was connected in place of the dropping mercury electrode and the potentiometer set to produce a convenient deflection of the galvanometer. A second smaller value of resistance was then chosen to produce a corresponding decrease in the deflection. The potentiometer was reset to produce the original

deflection. From this data the current was readily calculated by Ohm's Law. For each particular setting of the galvanometer shunt the sensitivity in microamperes per millimeter was then found. The sensitivity was determined to be 0.018 microampere per mm. at three different settings of the galvanometer shunt.

Experimental Procedure. The mercury reservoir was adjusted to a height of 52 cm. above the desk top to give a drop time of four seconds throughout the experiment.

Vibrations affecting the galvanometer deflection were markedly reduced by the use of a Fisher "Vibradamp", a heavy metal plate mounted on sponge rubber blocks.

Since the presence of dissolved oxygen causes an undesirable increase in the residual current, (12) commercial hydrogen was used to flush all solutions before electrolysis. The hydrogen was bubbled through the solution in the cell for thirty minutes before beginning the electrolysis and the gas outlet tube was then adjusted to blanket the surface of the solution in order to prevent absorption of the oxygen from the atmosphere..

In the "Fisher" Elecdropode" no provision is made for thermostating the cell. For accurate work and particularly in a theoretical investigation, it is considered necessary to control the temperature of the cell to within ± 0.5 °C in order to keep variations in the diffusion current within ± 1 per cent. (13) For an initial survey of the type undertaken here, however, control of temperature was dispensed with.

During the period in which these measurements were made, the temperature of the laboratory was fairly constant at 24° C.

Instrument Accuracy. To check the accuracy of the "Elecdropode" an ion whose half-wave potential was recorded in the literature was electrolyzed. A solution of cadmium ion in 1 N potassium chloride was found to have a half-wave potential of 0.65. The value stated in the literature is - 0.64 v. vs. the saturated calomel electrode. (14) Since the nickel ion is under consideration here, a solution of 0.001 M nickel chloride hexahydrate in 1 N potassium chloride was electrolyzed. The half-wave potential is - 1.09 v. vs. the saturated calomel electrode; this is in good agreement with the literature value of - 1.1 v. vs. the saturated calomel electrode. (15). Fig.3 shows the irreversible reduction of the nickel hexaquo ion.

IV. AQUEOUS ETHYL ALCOHOL AS SOLVENT

In studying the polarographic behavior of this group of nickel chelates, there was considerable difficulty in selecting a suitable solvent. Nickel disalicylaldehyde and its derivatives are to a large extent insoluble in the more common solvents. Although pyridine was known to be one of the best solvents for compounds of this type, other solvents having dielectric constants suitable for this work were sought since pyridine is known to form a complex with nickel ion. (16) Formation of such a complex in the solution is one more factor to consider in any attempt to rationalize the behavior of the nickel chelates.

First, a mixture of ethyl alcohol and water, 50% by volume, was tried. Preliminary experiments to determine the factors affecting the residual current of a supporting electrolyte of 0.1 N potassium chloride in 50% by volume aqueous alcohol indicated that either reducible substances in the alcohol or in the indifferent salt could be responsible for the large magnitude of the residual current. Curve a in Fig. 1 shows this blank.

Substitution of Baker's C. P. potassium nitrate for the salt used before did not improve the behavior any. Consequently, the ethyl alcohol was purified by the method of Danner and Hildebrand (17) by distilling over silver oxide. A blank on this sample showed a considerable improvement over the previous case with the greater portion of the curve

IV. AQUEOUS ETHYL ALCOHOL AS SOLVENT

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First, a mixture of ethyl alcohol and water, 60% by volume, was tried. Preliminary experiments to determine the factors affecting the residual current of a supporting electrolyte of 0.1 N potassium chloride in 60% by volume aqueous alcohol indicated that either reducible substances in the alcohol or in the indifferent salt could be responsible for the large magnitude of the residual current. Curve a in Fig. 1 shows this blank.

Substitution of Baker's C. P. potassium nitrate for the salt used before did not improve the behavior any. Consequently, the ethyl alcohol was purified by the method of Danner and Hildebrand (17) by distilling over silver oxide. A blank on this sample showed a considerable improvement over the previous case with the greater portion of the curve constant at 0.9 microamp. as compared to -1.4 microamp. for the untreated alcohol. Below - 1.0 v. however, the current rose to 1.2 microamp. (102 units). (Fig. 1b).

A second distillation over silver oxide and fractionation through a four foot column packed with glass beads brought about no further improvement in the characteristics of the alcohol.

Increasing the amount of purified ethyl alcohol in the supporting electrolyte caused a proportionate increase in the residual current showing that the large residual current is due to the use of alcohol in the supporting electrolyte. (Fig.4). Since repeated distillation over silver oxide did not lower the current, we are forced to conclude that the increased solubility of oxygen in alcohol is responsible for the increase in the diffusion current. Fig.2 shows the manner in which the addition of alcohol increases the residual current of an aqueous solution. In this same connection, Fig. 2 is of interest since it shows the effect of increasing the time of flushing a solution with hydrogen. The marked decrease in the residual current when the time is doubled is evidence that most of this current is due to the presence of dissolved oxygen.

To determine the half-wave potential of nickelous ion in 50% by volume aqueous alcohol a 0.0001 M nickel nitrate hexahydrate solution in 0.1 N potassium nitrate was electrolyzed. Fig. 5 shows the half-wave potential in this medium to be - 1.08 v. (Fig. 5).

Fig. 1.

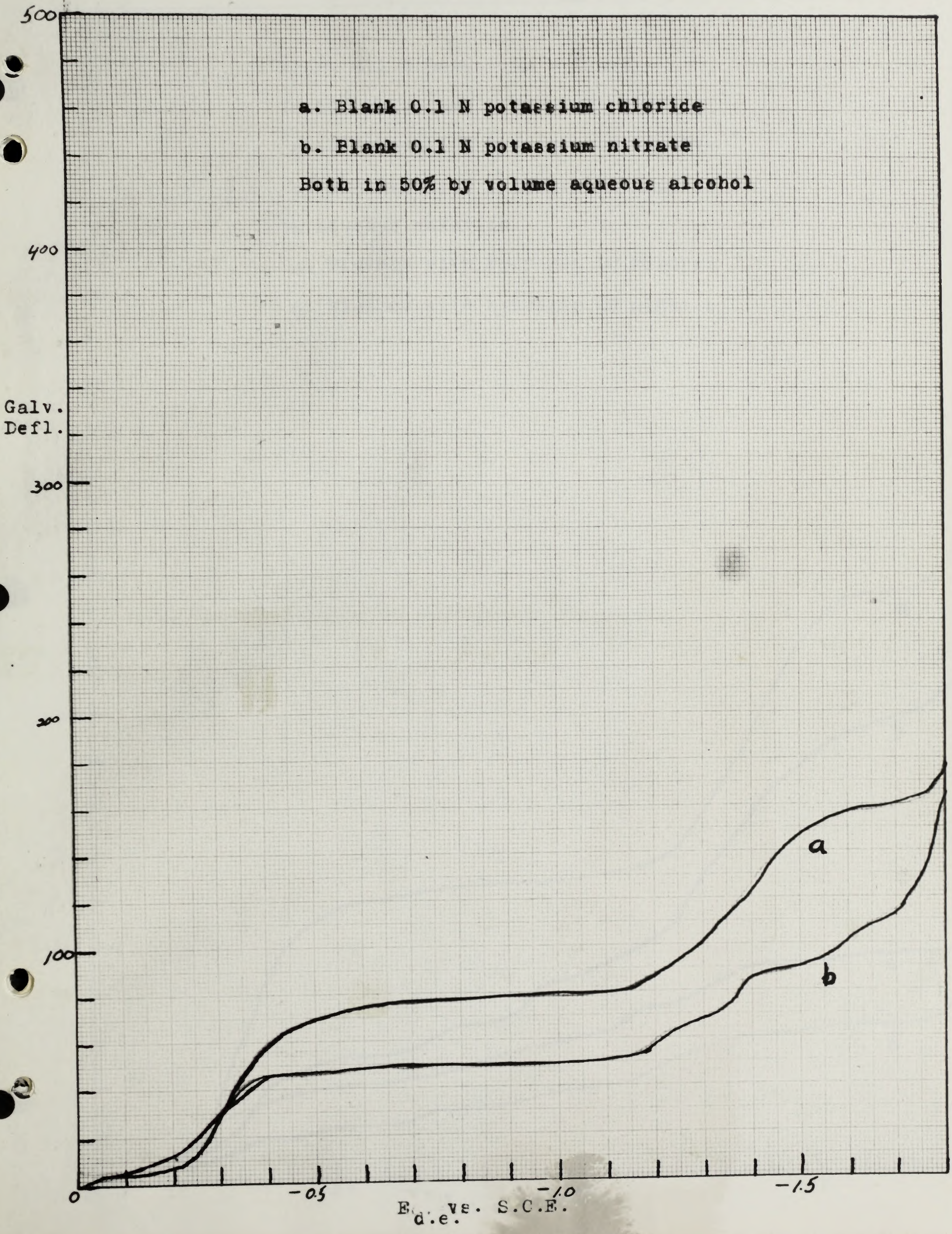

a. Blank 0.1 N potassium chloride
b. Blank 0.1 N potassium nitrate
Both in 50% by volume aqueous alcohol
500
400
300
200
100
0
Galv. Defl.
-0.5
-1.0
-1.5
$E_{d.e.}$ vs. S.C.E.
a
b

Fig.2

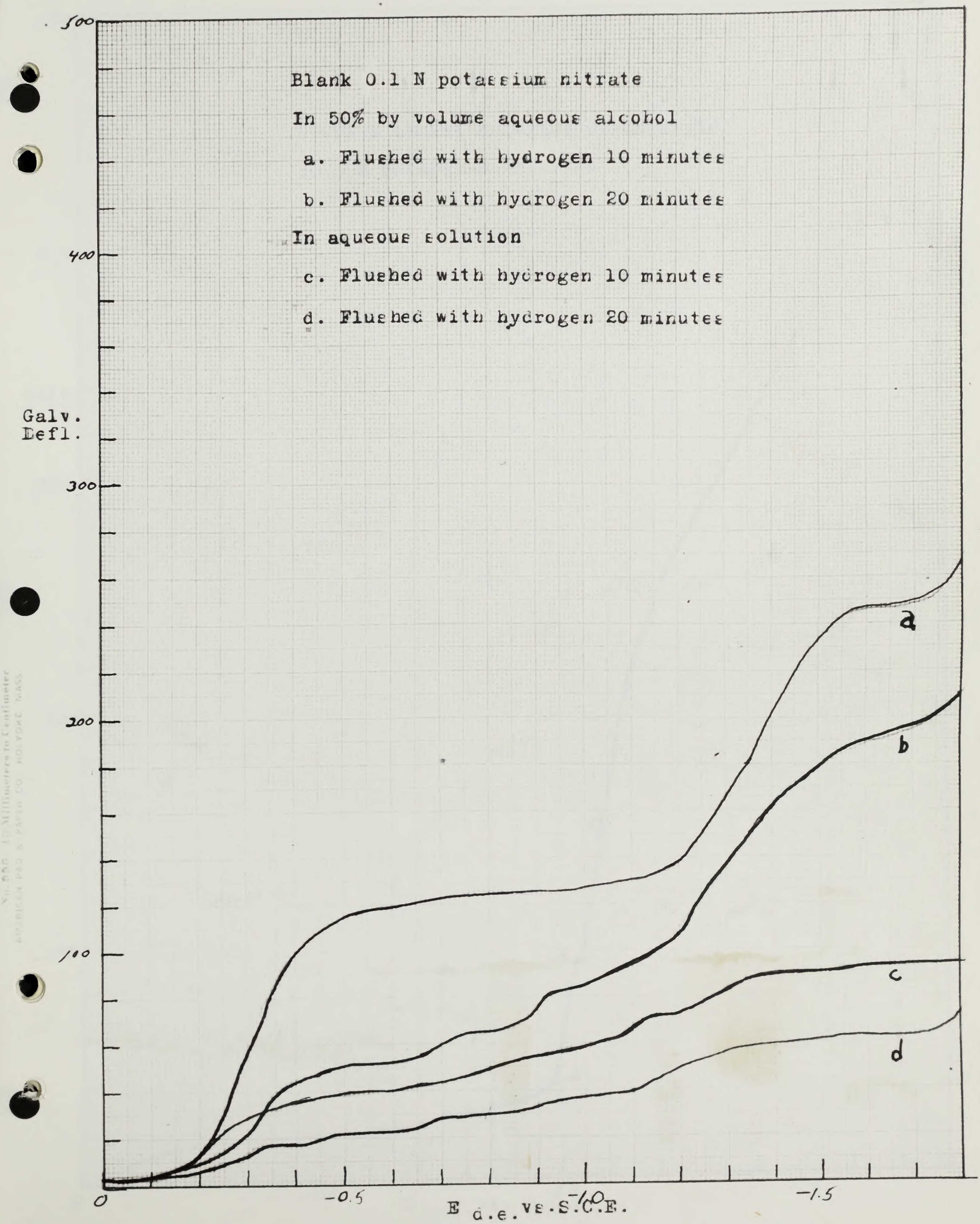

Blank 0.1 N potassium nitrate
In 50% by volume aqueous alcohol
a. Flushed with hydrogen 10 minutes
b. Flushed with hydrogen 20 minutes
In aqueous solution
c. Flushed with hydrogen 10 minutes
d. Flushed with hydrogen 20 minutes
Galv. Defl.
500
400
300
200
100
0
-0.5
-1.0
-1.5
E d.e. vs. S.C.E.
a
b
c
d

Fig.3

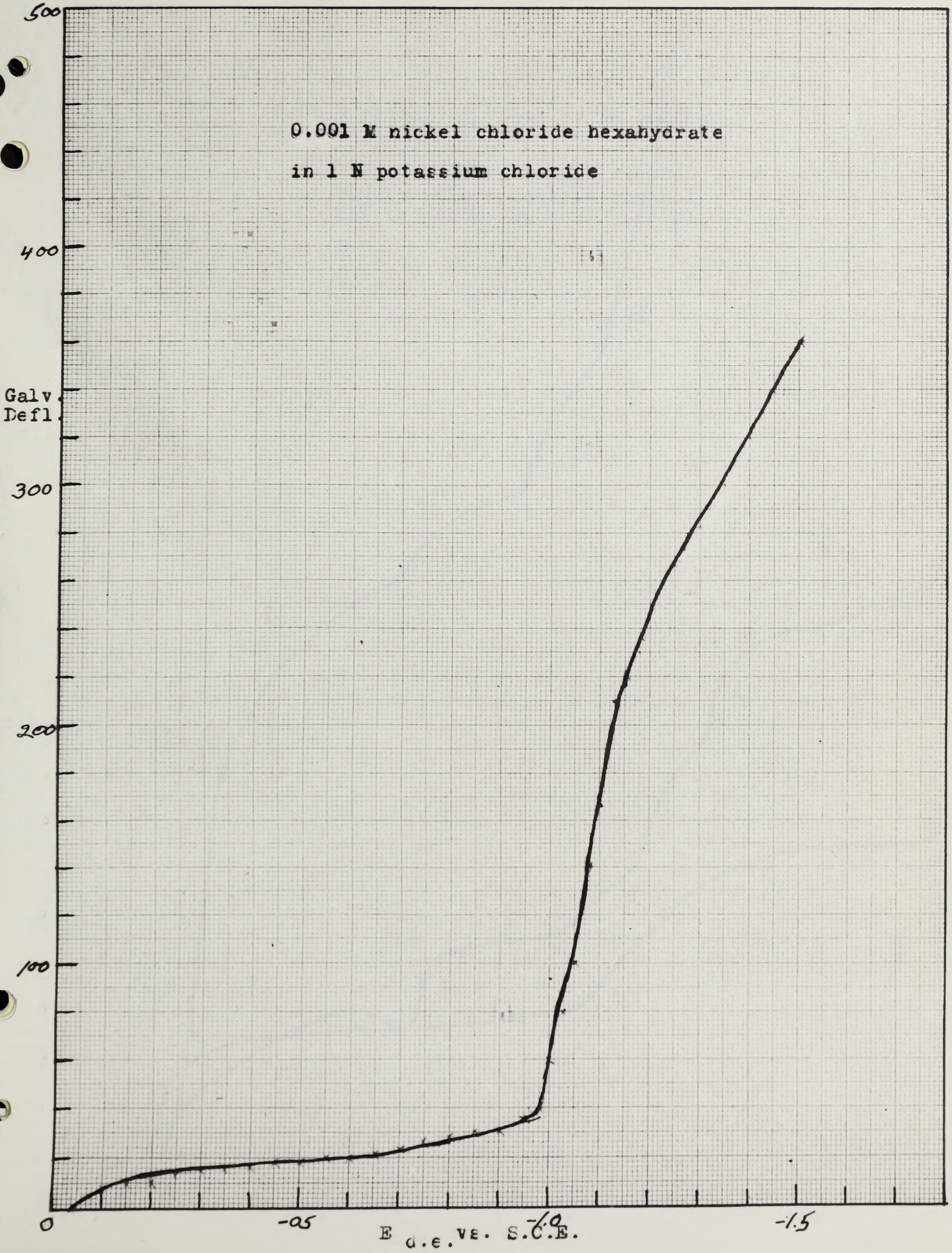
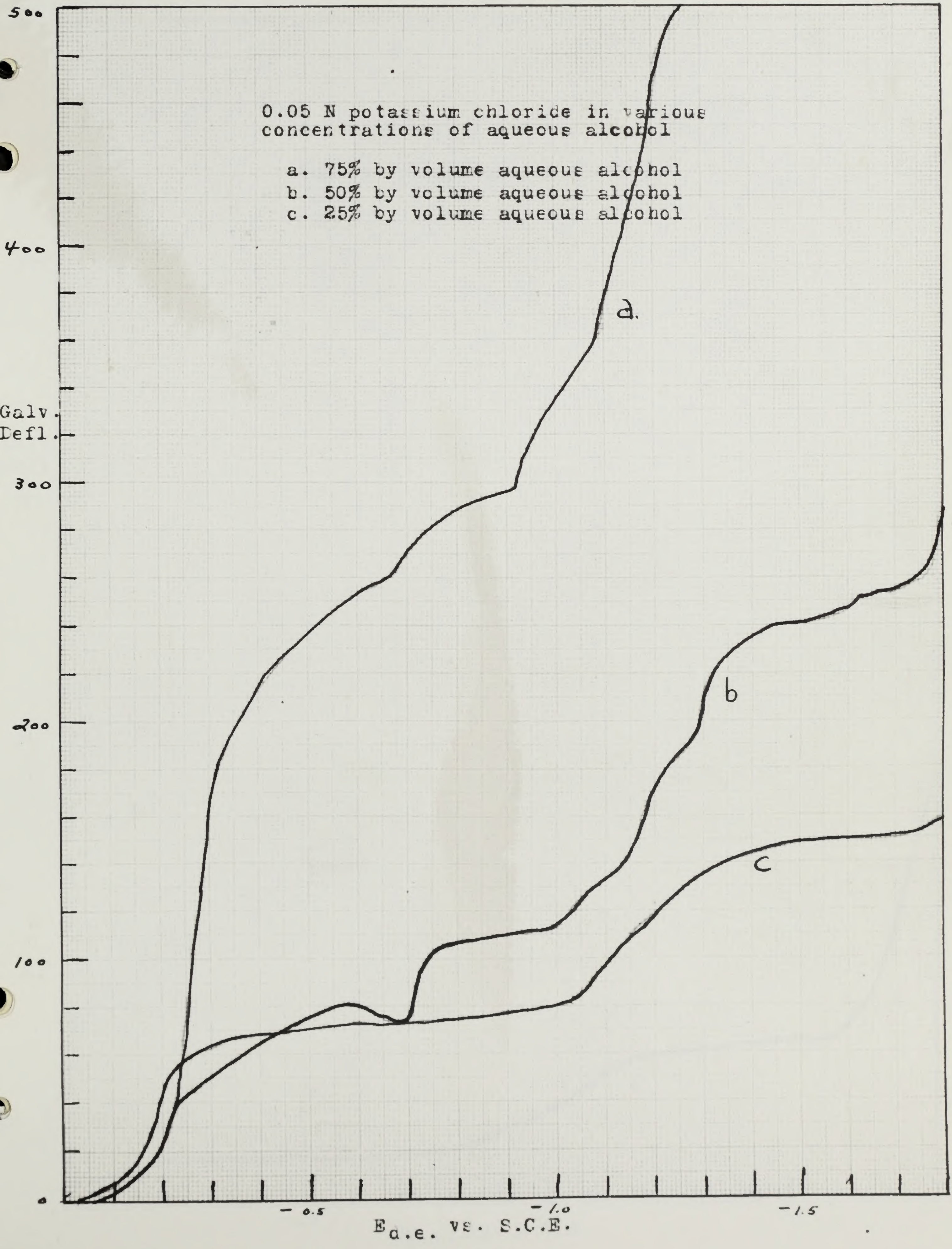

0.001 M nickel chloride hexahydrate
in 1 N potassium chloride
500
400
300
200
100
Galv.
Defl.
0
-0.5
-1.0
-1.5
E d.e. vs. S.C.E.

Fig. 4



0.05 N potassium chloride in various concentrations of aqueous alcohol

a. 75% by volume aqueous alcohol
b. 50% by volume aqueous alcohol
c. 25% by volume aqueous alcohol

Fig. 5

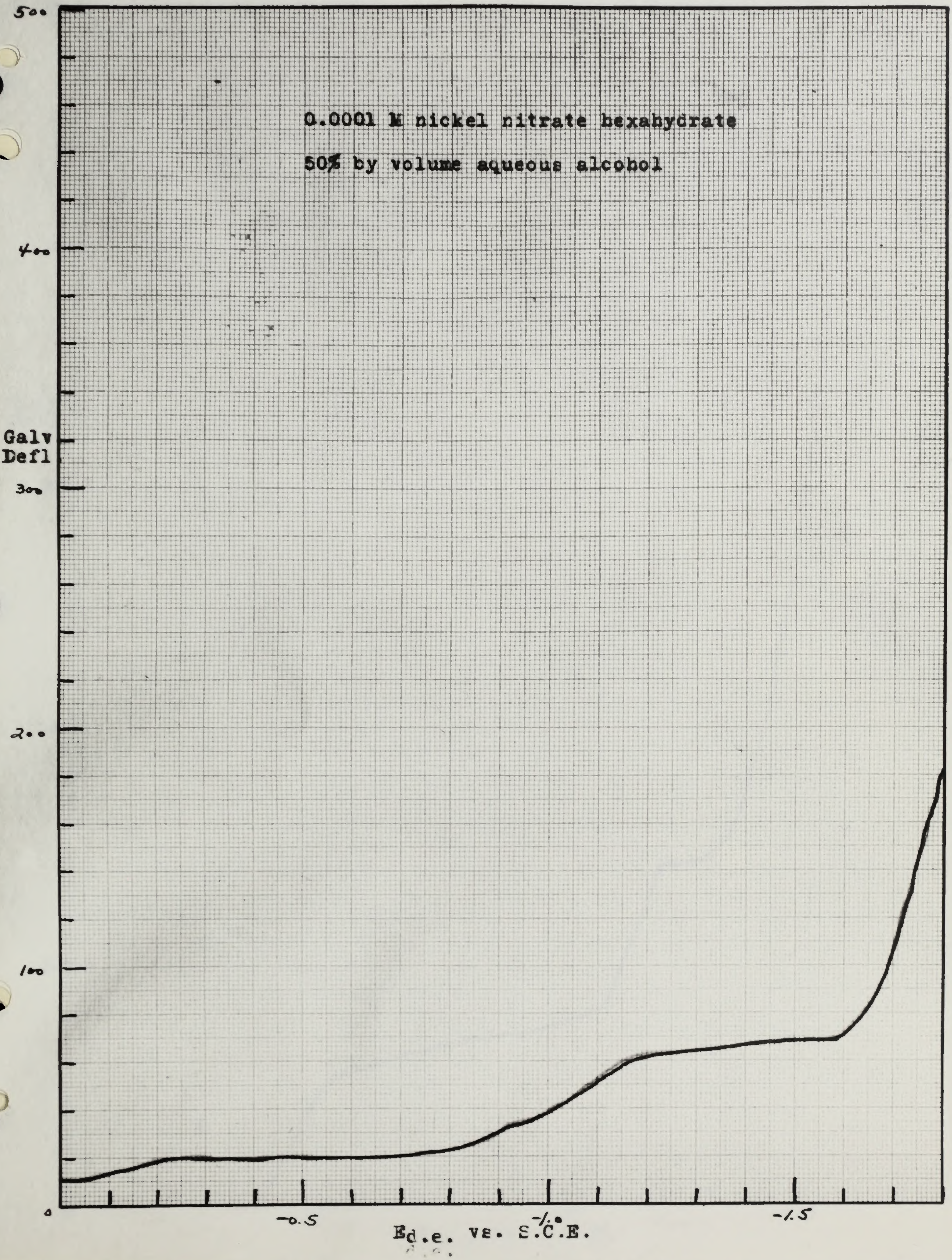
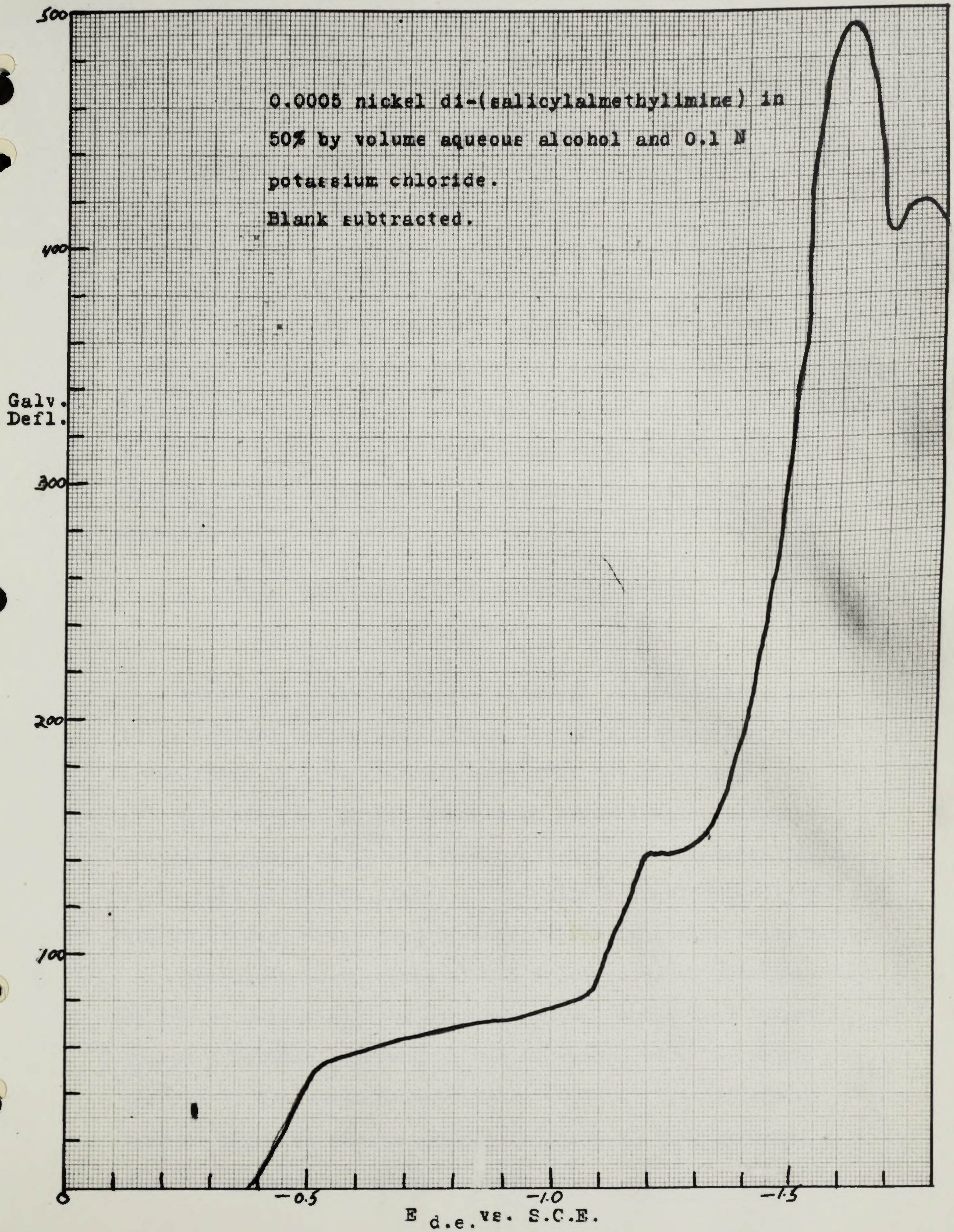

0.0001 M nickel nitrate hexahydrate
50% by volume aqueous alcohol
500
400
Galv Defl
300
200
100
0
-0.5
-1.0
-1.5
$E_{d.e.}$ vs. S.C.E.

Fig. 6



0.0005 nickel di-(salicylalmethylimine) in 50% by volume aqueous alcohol and 0.1 N potassium chloride.
Blank subtracted.
500
400
300
200
100
0
Galv. Defl.
-0.5
-1.0
-1.5
E d.e. vs. S.C.E.

The polarogram of a 0.0005 M nickel di-(salicylalmethylimine) solution in 50% by volume aqueous alcohol and 0.1 N potassium nitrate was determined but the magnitude of the residual current was so great as to cast considerable doubt upon the accuracy of significant portions of the curve. (Fig.6)

Because of the difficulties of obtaining a blank having a small enough residual current, the use of ethyl alcohol was abandoned. Furthermore, when we consider that the nickel di-(salicylalmethylimine) was soluble only to the extent of 0.0005 M, it is doubtful that effective concentrations of the higher members of the series could be obtained in this medium since they are even less soluble generally.

III. ETHYLENE GLYCOL MONOMETHYL ETHER AS SOLVENT

Since the nickel disalicylaldehyde compounds were known to be soluble in ethylene glycol monomethyl ether, the characteristics of this compound were next investigated.

The ethylene glycol monomethyl ether available was of practical grade so it was fractionated in a column having the equivalent of thirty plates. The middle fraction boiling 121-122.5 deg. C was used throughout the following experiments.

The blank c.-v. curve of 0.1 N potassium nitrate solution in 50% by volume aqueous ethylene glycol monomethyl ether showed a residual current of 0.6 microamp. over the major portion of the curve commencing at -0.3 v. The diffusion current began to rise sharply at -1.3 v. to 1.6 microamp. (135 units) before reduction of the potassium ion commenced

to take place at - 1.8 v. It was also noted that potassium nitrate was less soluble in 50% by volume aqueous ethylene glycol monomethyl ether than in 50% by volume aqueous alcohol.

Potassium chloride was next investigated to determine if it had more desirable characteristics. The c. -v. curve of a potassium chloride blank was found to be very similar to that of potassium nitrate.

Since lithium chloride exhibits the valuable property of being extremely soluble in water to the extent of 65 parts in 100, it was next tried as the indifferent salt. The c. -v. curve of a lithium chloride blank shows the residual current remaining at 0,4 microamp. from -0.3 v. to -1.2 v. at which point it rises gradually to 0.4 microamp. (35 units). (Fig. 7). Here we have a considerable improvement over the other salts tested.

A blank of lithium nitrate showed it to have similar properties in ethylene glycol monomethyl ether-water mixtures.

In the experiments discussed below lithium chloride was used as the indifferent salt and 50% by volume ethylene glycol monomethyl ether was used as the solvent. In preparing solutions, the organic chelate compound was first dissolved in the organic solvent, and then the required amount of lithium chloride added as a 0.5 N lithium chloride solution. The volumetric flask was then made up to the mark with distilled water. All attempts to dissolve the chelates directly in the 50% by volume aqueous ethylene glycol monomethyl ether were unsuccessful.

For purposes of comparison with the nickel chelates a 0.0005 M nickel nitrate hexahydrate solution was electrolyzed. In this medium the half-wave potential of the nickel hexaquo ion is found to be - 1.23 v. vs. the saturated calomel electrode. The limiting current is 2.2 microamp. after subtraction of the blank. Nickel has a prominent maximum even in dilute solutions which must be suppressed to reveal the true form of the curve. In this case two ml. of a 0.5% gelatin solution were added to 100 ml. of solution to make the final concentration 0.01%. This concentration is sufficient to suppress the maximum without depressing the diffusion current. (18)

The c. -v. curve of 0.0005 M nickel di-(salicylalmethylimine) solution shows a first step whose half-wave potential can be determined as - 1.18 v. vs. the saturated calomel electrode. (Fig. 10). The limiting current of this step after subtraction of the blank is 1.8 microamp. (150 units). The remainder of the curve is more difficult to interpret correctly because of the existence of a slight maximum that distorts the curve. Gelatin was used in a concentration of 0.01% to suppress this maximum. If we consider the remainder of the curve as a single step, we find that it has a half-wave potential of approximately - 1.6 v. vs. the S.C.E.

The c.-v. curve of a 0.0005 M nickel di-(salicylaldimine) solution was found to be much different (Fig. 9). It is difficult to determine the half-wave potential of this curve exactly since the steps are poorly defined and the diffusion current very small. The well-defined first step is noticeably absent.

Attempts to prepare a 0.0005 M solution of nickel di-(salicylal)-pentamethylenediimine failed. If the polarograms of the other members of the series were to be determined, a higher concentration of the organic solvent would be necessary to dissolve the nickel chelates.

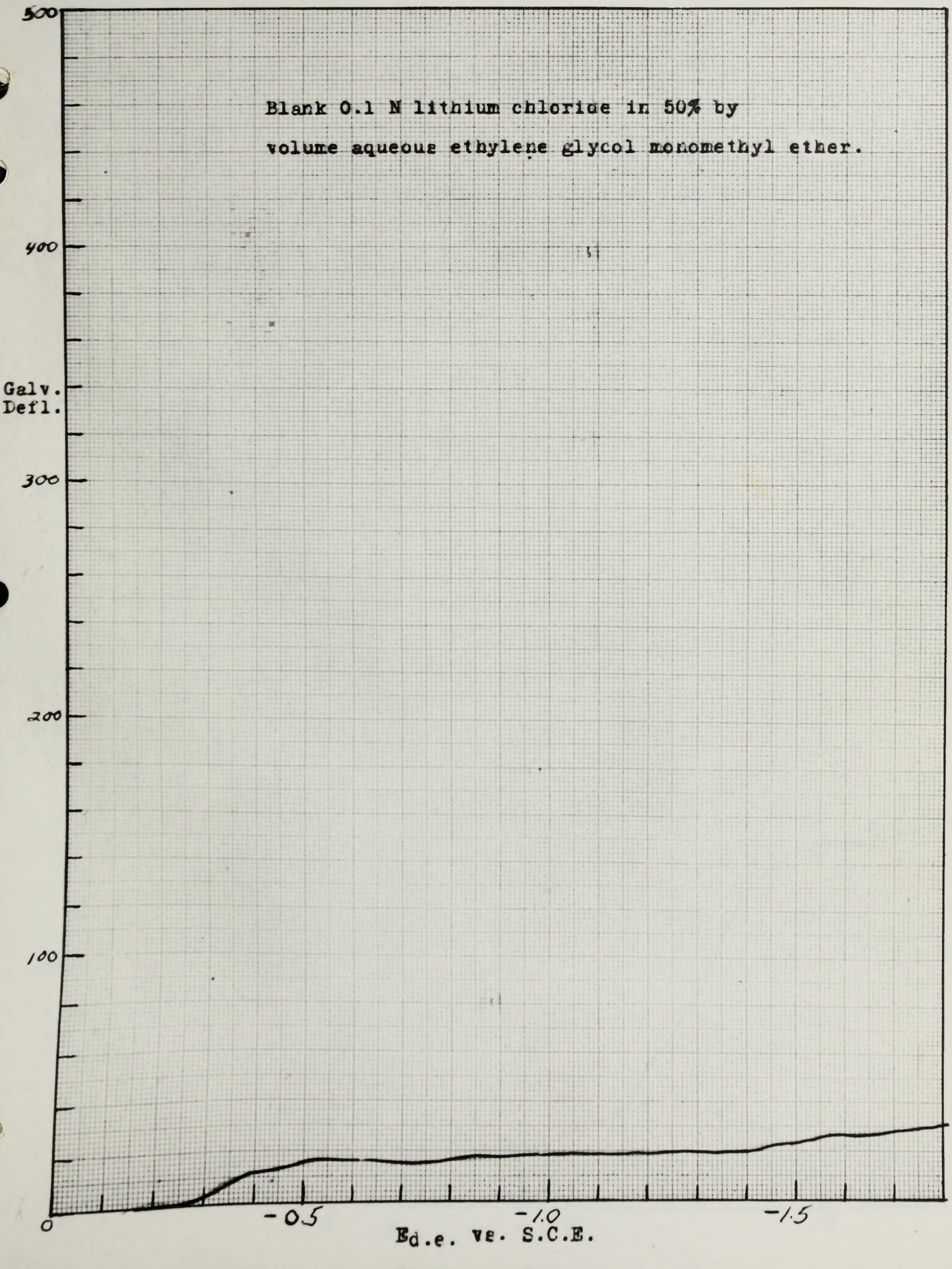
A blank of 0.1 N lithium chloride in 75% by volume ethylene glycol monomethyl ether had a residual current nearly double that of the 50% mixture. It was thought, however, that the increase might be tolerated if the increase in solubility of the chelates was sufficiently great.

A c.-v. curve of a 0.0005 M nickel di-(salicylalmethylimine solution is 75% by volume aqueous ethylene glycol monomethyl ether was exactly like that of the same compound in a 50% mixture except that the residual current was so much greater in relation to the diffusion current.

No additional information was gained from consideration of the polarogram of nickel di-(salicylaldimine) in 75% by volume aqueous ethylene glycol monomethyl ether.

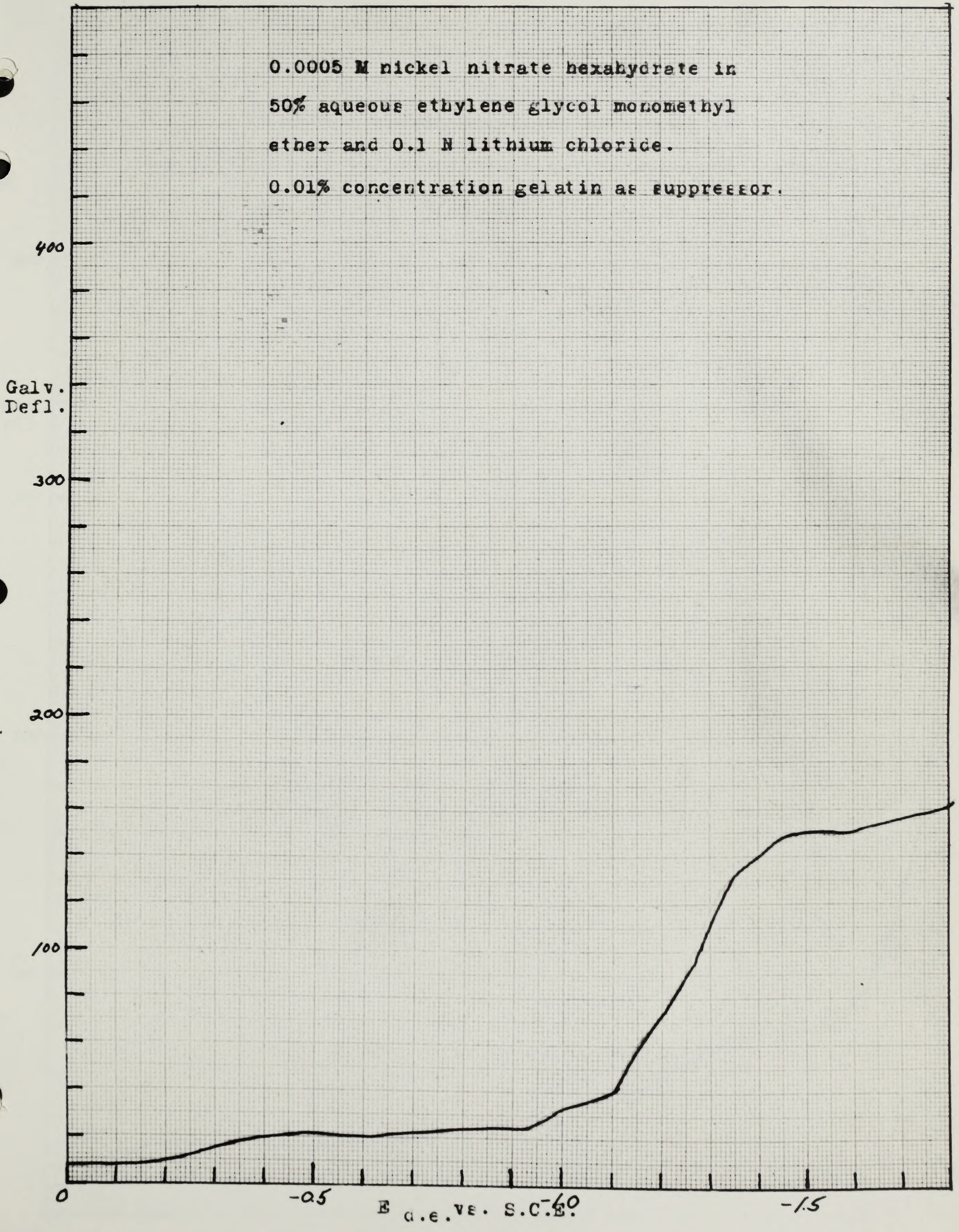
Electrolysis of a 0.00025 M nickel di-(salicylal)-pentamethylenediimine solution produced a curve to which

Fig. 7



Blank 0.1 N lithium chloride in 50% by volume aqueous ethylene glycol monomethyl ether.

Fig. 8

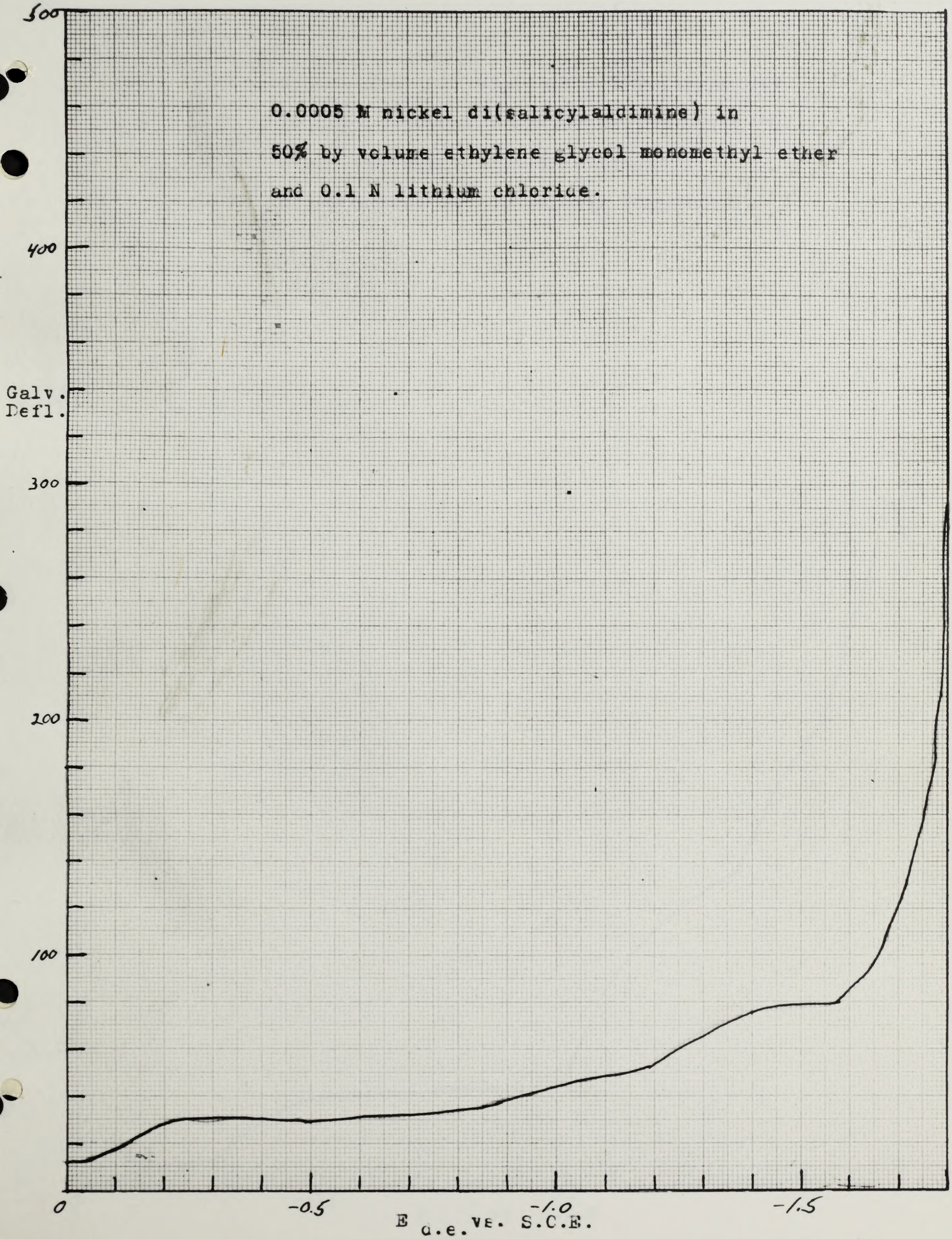


0.0005 M nickel nitrate hexahydrate in 50% aqueous ethylene glycol monomethyl ether and 0.1 N lithium chloride.

0.01% concentration gelatin as suppressor.

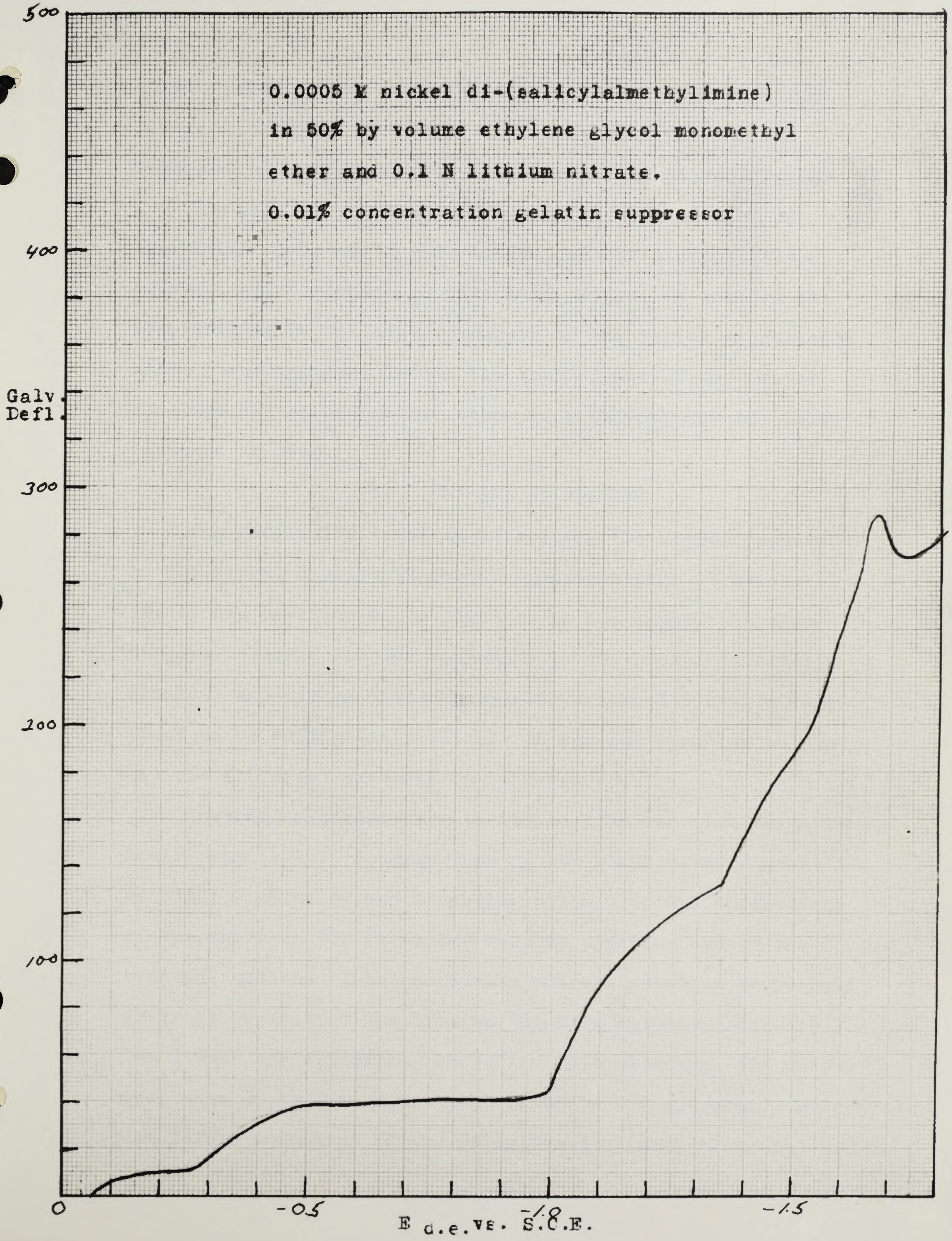
No. 330—10 Millimeters to Centimet

Fig. 9



0.0005 M nickel di(salicylaldimine) in 50% by volume ethylene glycol monomethyl ether and 0.1 N lithium chloride.

Fig. 10


0.0005 M nickel di-(salicylalmethylimine)
in 50% by volume ethylene glycol monomethyl
ether and 0.1 N lithium nitrate.
0.01% concentration gelatin suppressor

little significance could be attached since the curve was nearly a straight line from -0.3 v. to -1.8 v. with the exception of a hump thought to be due to dissolved oxygen.

The lack of well-defined steps in the reduction of the nickel chelates in this medium and the difficulties experienced in removal of dissolved oxygen, as well as the insolubility of the higher members of the series of chelates under investigation, led to the abandonment of the use of ethylene glycol monomethyl ether as a colvent for the polarographic studies.

IV, PYRIDINE AS SOLVENT

The difficulty found in dissolving the higher members in the nickel disalicylaldehyde compounds made it necessary to use pyridine-water mixtures as the supporting electrolyte. Nearly all the compounds in the nickel disalicylaldehyde and nickel di(3-ethoxysalicylaldehyde) series were found to be sufficiently soluble in aqueous pyridine to permit the diffusion currents to be measured.

Several compounds were tested to find the most suitable indifferent salt. A comparison of the blank c.-v. curves of lithium chloride and potassium nitrate on 0.1 N solutions of the salts in 50% by volume aqueous pyridine showed the residual current of the potassium nitrate solution to be half as great as that of the lithium chloride solution (Fig. 11). The former has a limiting current of 0.5 microamp. (60 units) over most of the range until it rises to 0.7 microamp. (84 units) just before reduction of the potassium ion takes place at -1.8 v.

In an attempt to further improve the characteristics of the supporting electrolyte, the pyridine was fractionated through a four foot column having the equivalent of thirty plates. A blank with the redistilled pyridine showed no improvement. In the subsequent experiments, the Baker's C.P. pyridine was used without further treatment.

First, the behavior of nickel ion was studied in this different type of supporting electrolyte. Various amounts of nickel acetate tetrahydrate were dissolved in 50 ml. of pyridine, 20 ml. of 0.5 N potassium nitrate added, and the solution made up to 100 ml. with distilled water. The differences in the behavior of nickel ion at several different concentrations are shown in Fig. 12. Note that in this case reducing the concentration does not eliminate the maximum until the solution is so dilute that the diffucion current is barely measurable. Because of the fact that the maximum does not disappear even in the most dilute solutions, the half-wave potential of the nickel-pyridine complex can only be estimated at -0.9 v. Addition of gelatin as a suppressor had no effect on this maximum although previously it was found to be effective on the maximum of the nickel hexaquo ion.

In making up the solution of the nickel chelates, the compound was first dissolved in the pyridine, 20 ml. of 0.5 N potassium nitrate solution added, and the solution made up to 100 ml. with distilled water.

It was found impossible to make stable solutions of nickel di-(salicylal)-trimethylenediimine and nickel di-(salicylal)-hexamethylenediimine. Although they could be dissolved in hot pyridine, they were thrown out of solution by the addition of water to the cooled pyridine solution.

The maximum in the curve of nickel di-(salicylalmethylimine) was partially suppressed by the addition of gelatin, but methyl red and thymol blue had no effect at all as suppressors. Gelatin, when added to the solution of nickel di-(salicylaldimine) caused an increase in the height of the maximum. Thymol blue, methyl red and basic fuchsin were also ineffective in suppressing the maximum of nickel ion. These agents are customarily used in slightly acid solutions since the cation form of the dye is nesessary. It was found in this work, though, that the pyridium ion was formed in slightly acid solutions as evidence by the steep rise in the curve at -1.5 v. In strongly acid solutions the nickel chelates decompose.

The ethoxy substituted nickel chelates were found to have the same c.-v. curves as their parent compounds with the exception of the nickel di-(3-ethoxysalicylal)-pentamethylenediimine which behaves anomalously. The polarogram of this last compound is reproduced in Fig. 19.

Fig. 11

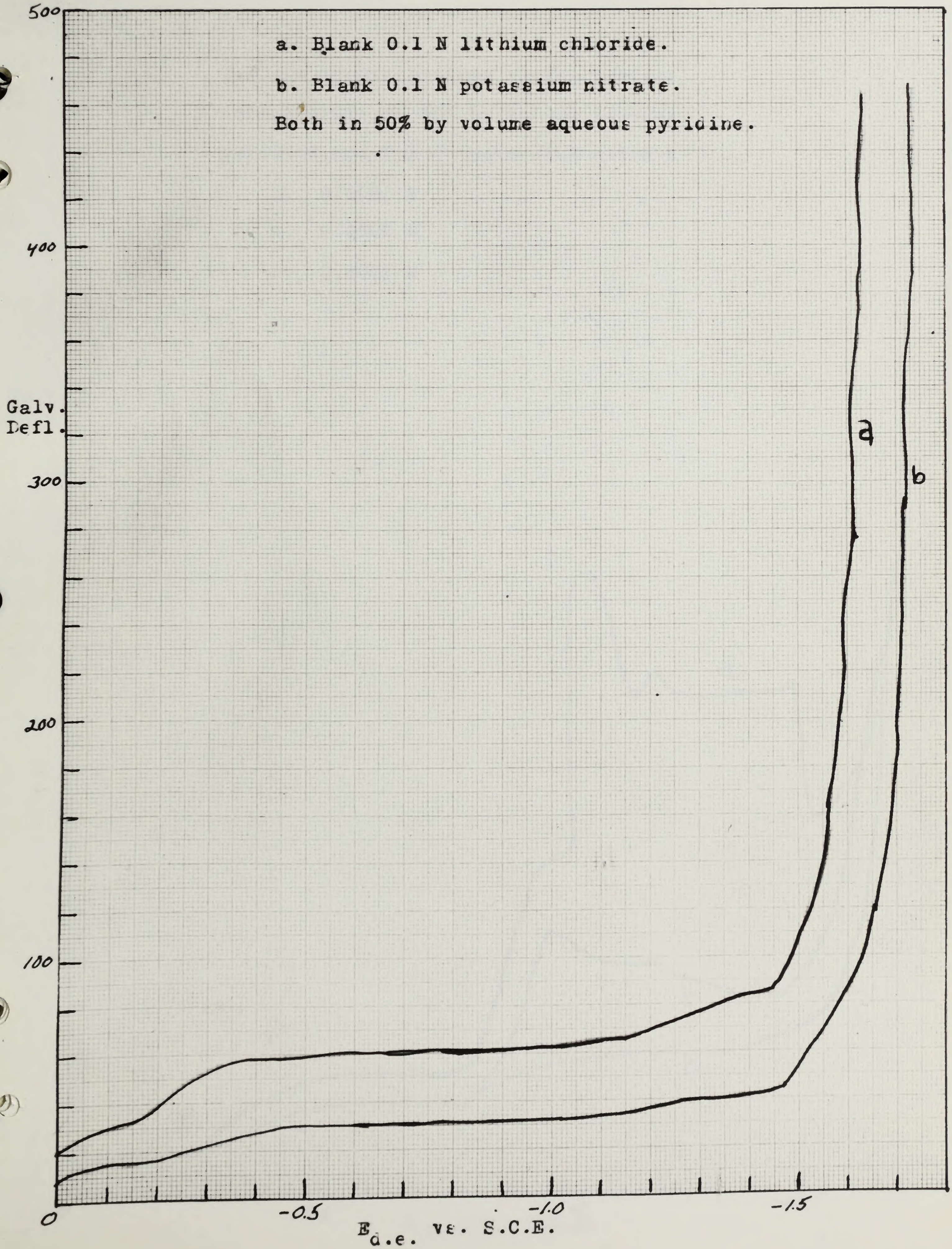

a. Blank 0.1 N lithium chloride.
b. Blank 0.1 N potassium nitrate.
Both in 50% by volume aqueous pyridine.
500
400
300
200
100
0
Galv. Defl.
-0.5
-1.0
-1.5
$E_{d.e.}$ vs. S.C.E.
a
b

Fig. 12

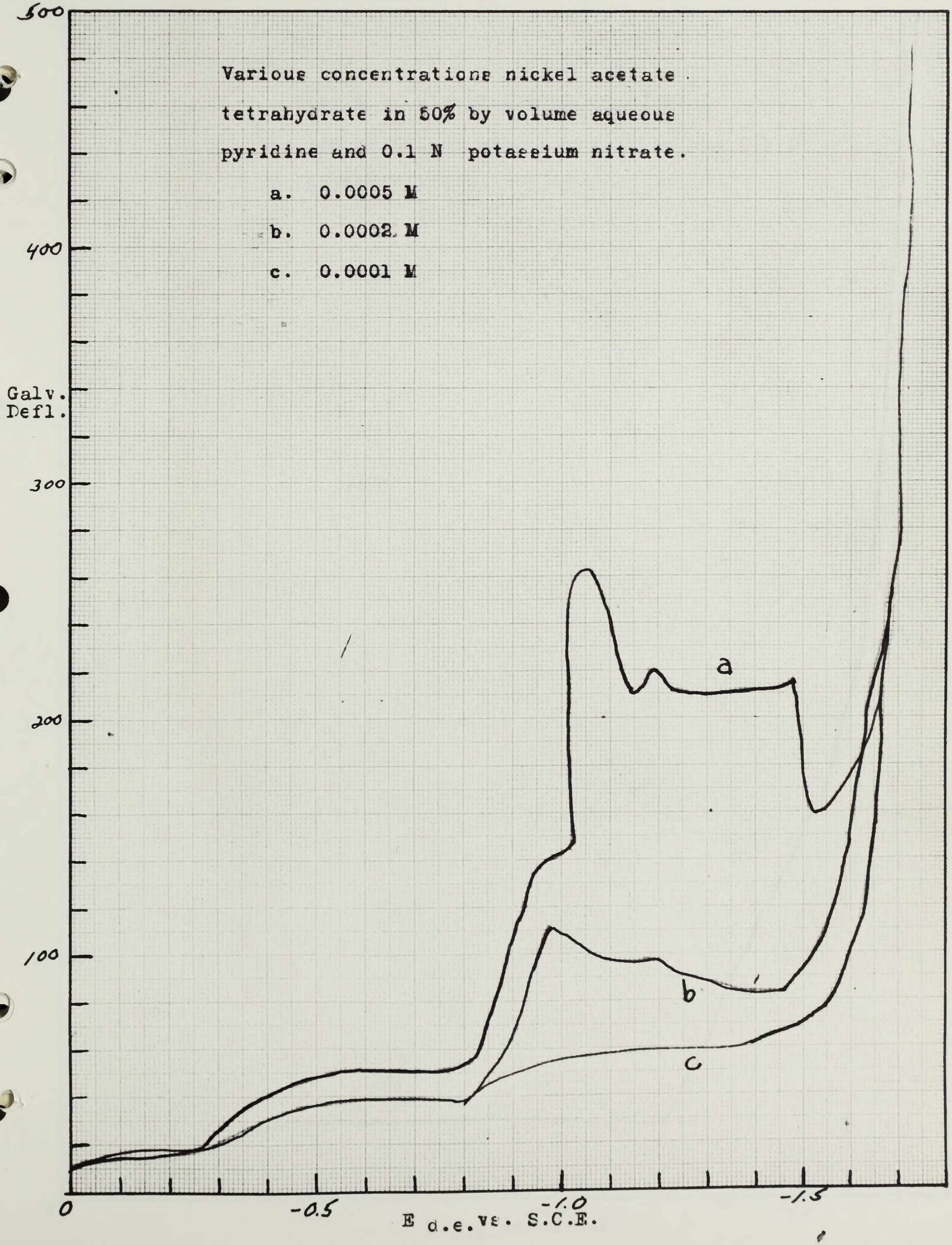
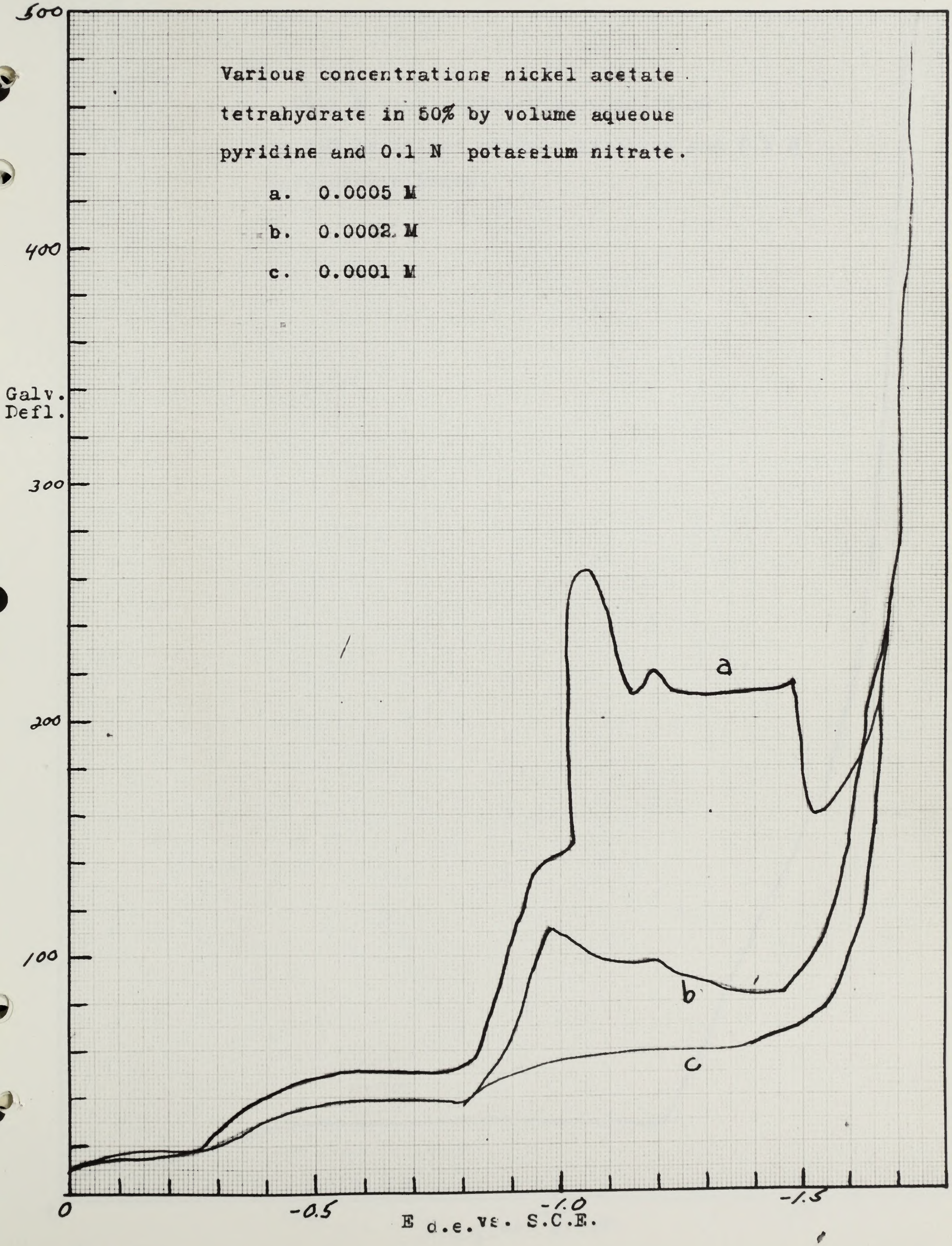

Various concentrations nickel acetate tetrahydrate in 50% by volume aqueous pyridine and 0.1 N potassium nitrate.
a. 0.0005 M
b. 0.0002 M
c. 0.0001 M
500
400
300
200
100
Galv. Defl.
0
-0.5
-1.0
-1.5
E d.e. vs. S.C.E.
a
b
c

Fig. 12



Various concentrations nickel acetate tetrahydrate in 50% by volume aqueous pyridine and 0.1 N potassium nitrate.

a. 0.0005 M

b. 0.0002 M

c. 0.0001 M

Fig. 13.

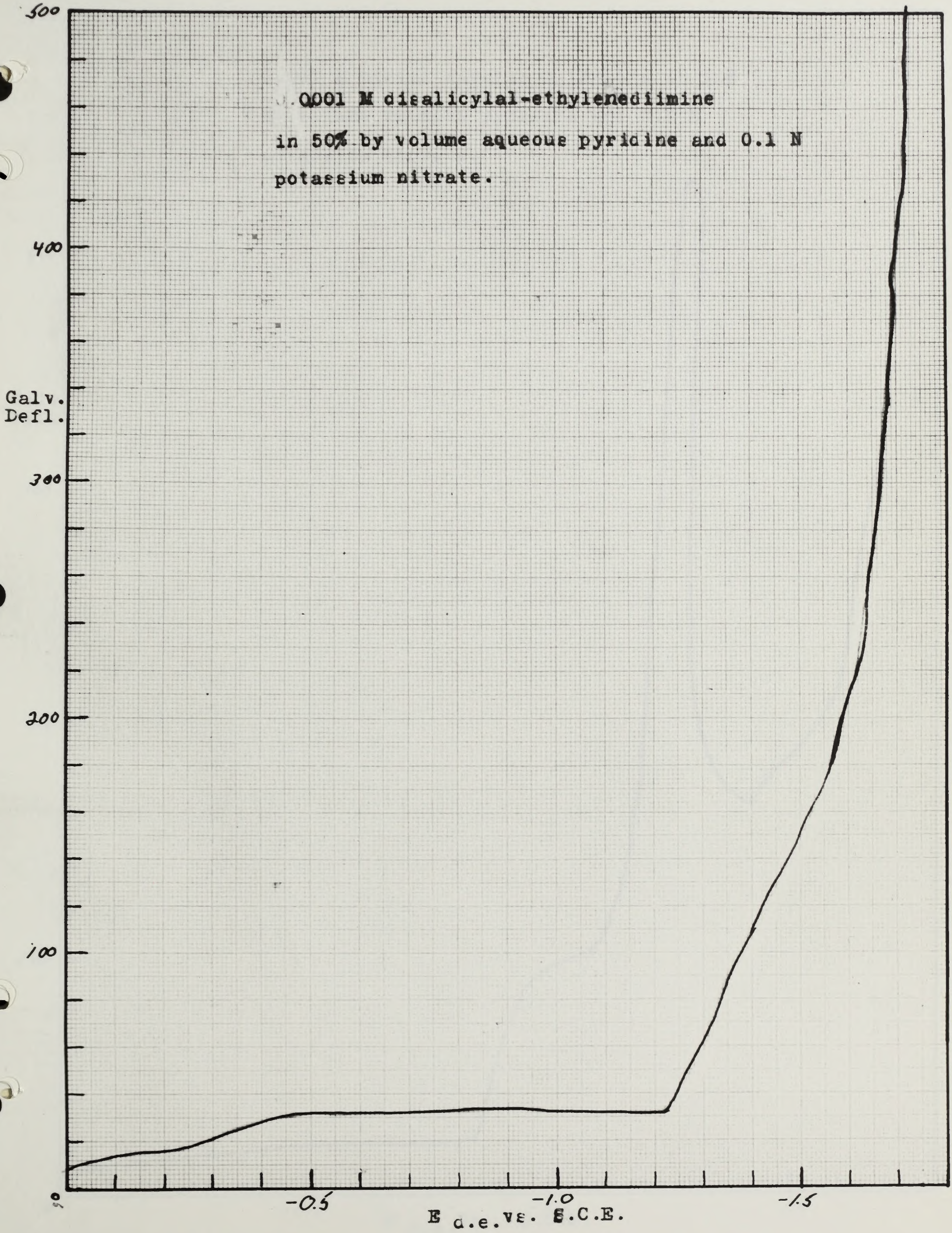
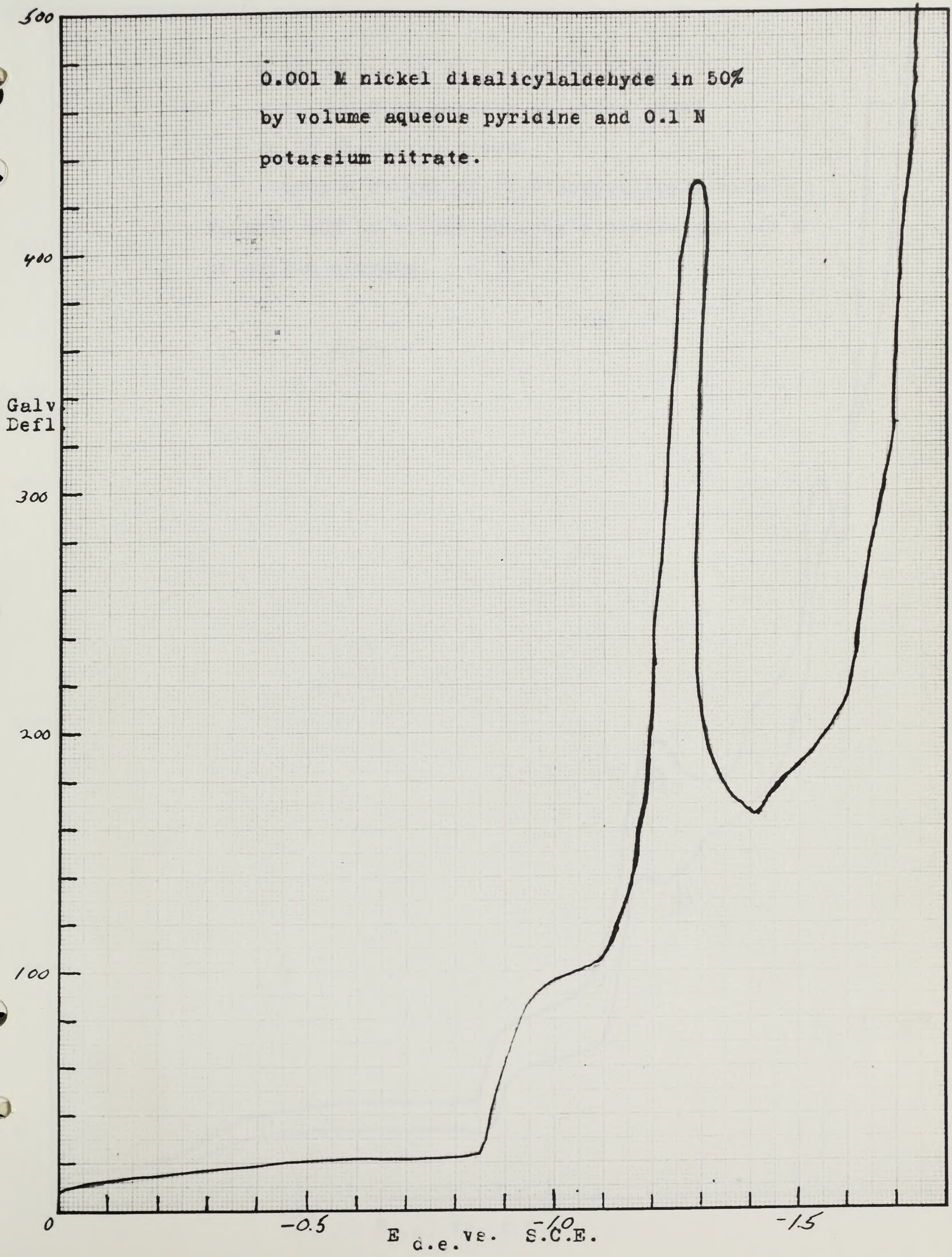
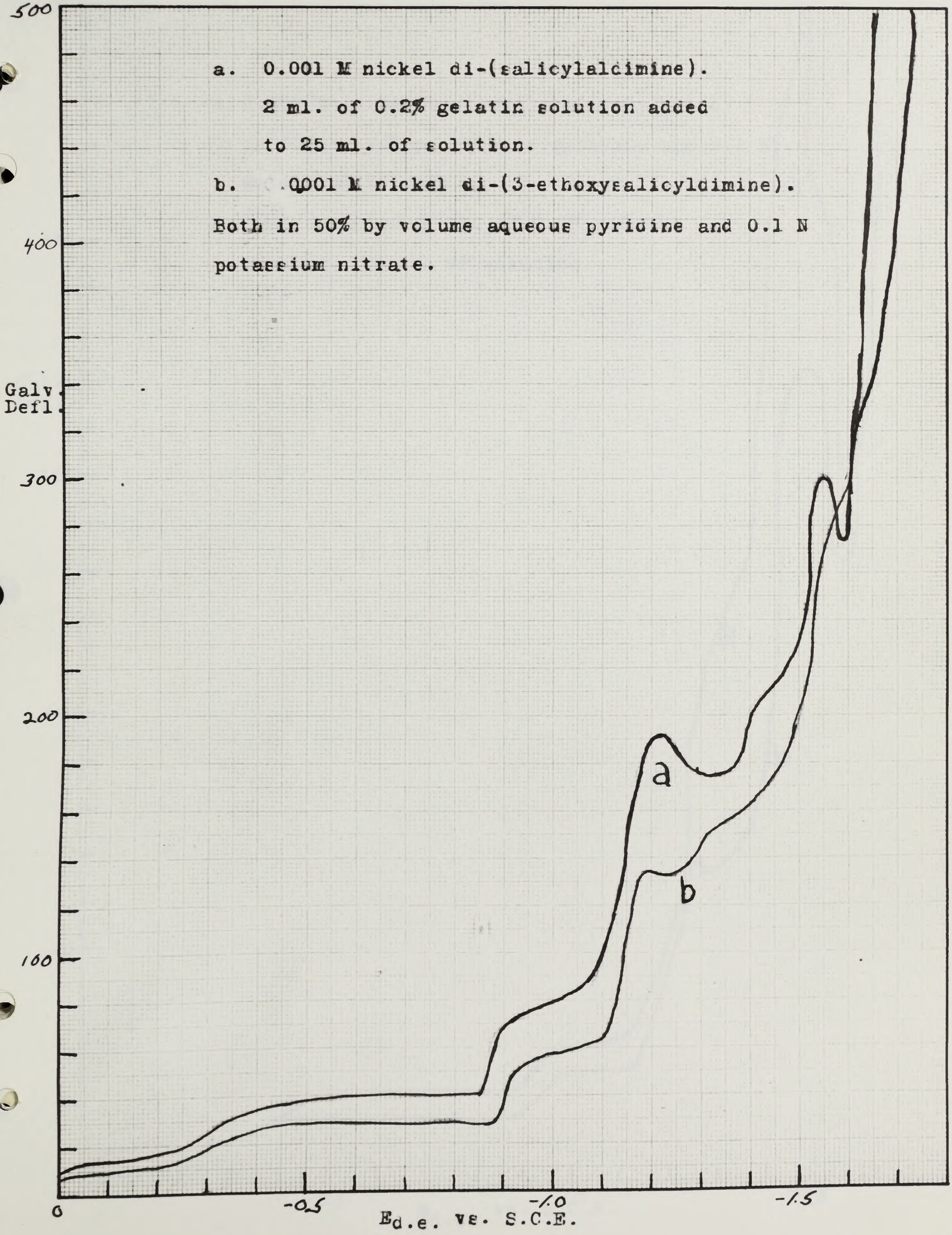

.0001 M disalicylal-ethylenediimine in 50% by volume aqueous pyridine and 0.1 N potassium nitrate.

Fig. 14



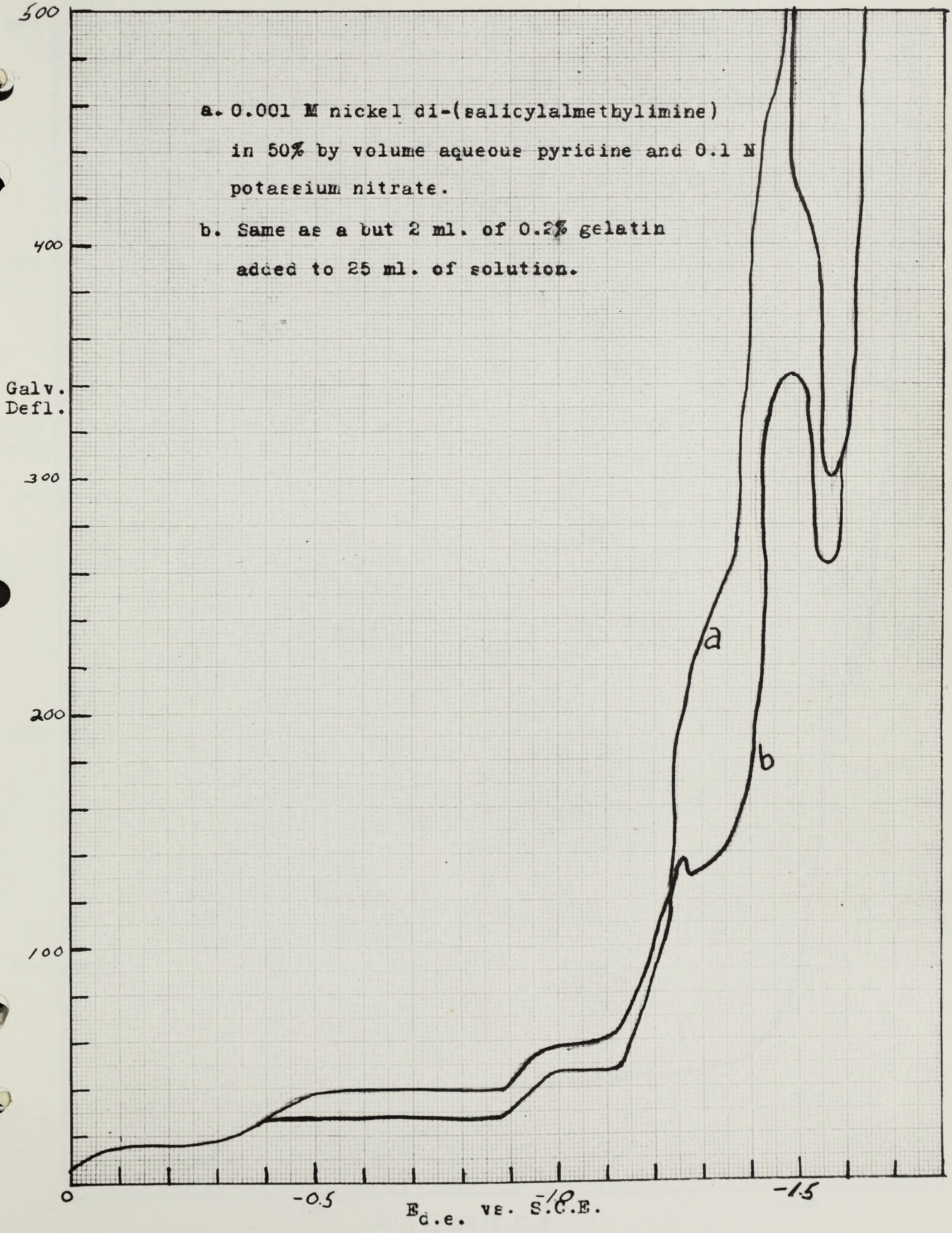
0.001 M nickel disalicylaldehyde in 50% by volume aqueous pyridine and 0.1 N potassium nitrate.

Fig. 15



a. 0.001 M nickel di-(salicylalcimine).
2 ml. of 0.2% gelatin solution added
to 25 ml. of solution.
b. 0.001 M nickel di-(3-ethoxysalicyldimine).
Both in 50% by volume aqueous pyridine and 0.1 N
potassium nitrate.

Fig. 16.



a. 0.001 M nickel di-(salicylalmethylimine) in 50% by volume aqueous pyridine and 0.1 N potassium nitrate.

b. Same as a but 2 ml. of 0.2% gelatin added to 25 ml. of solution.

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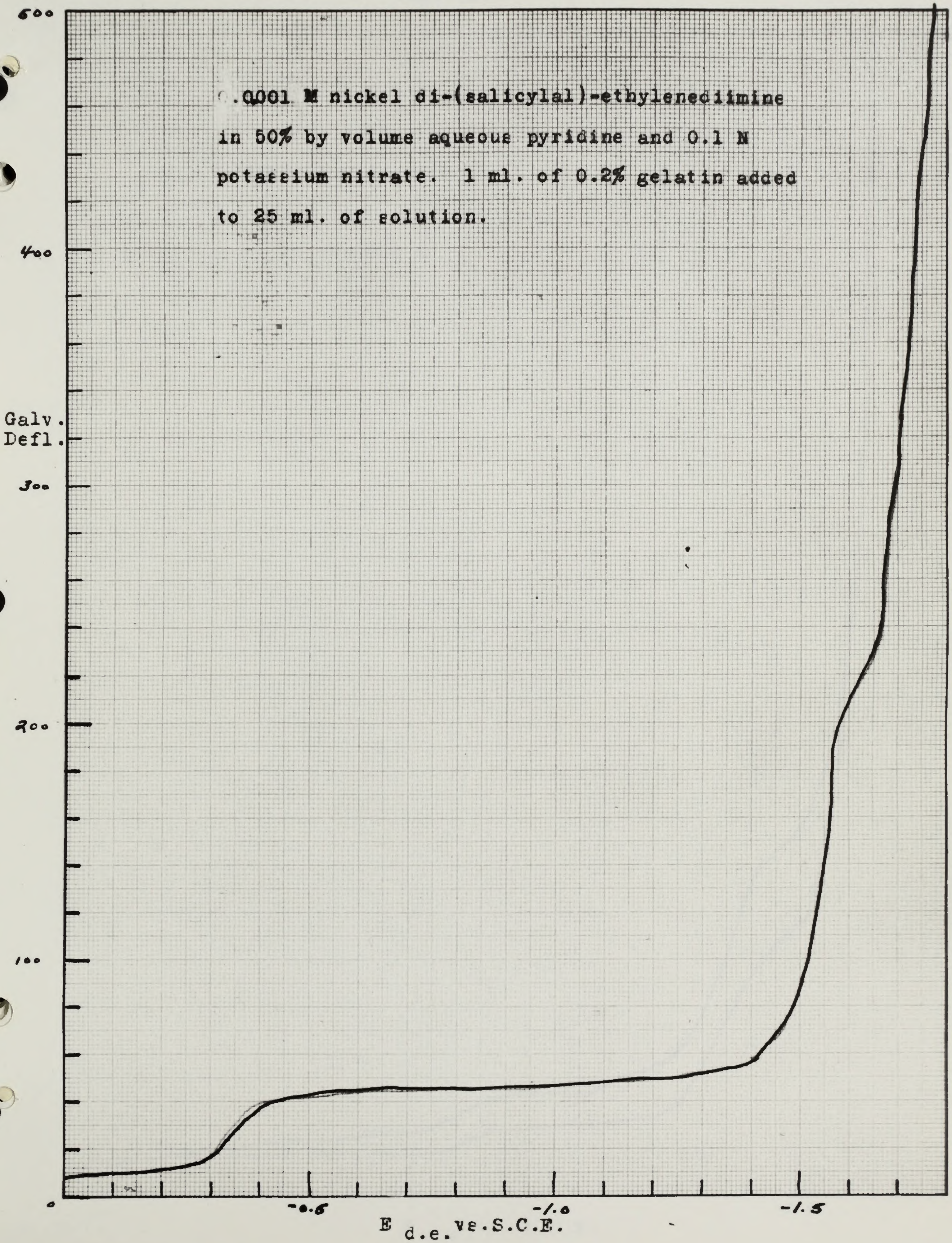
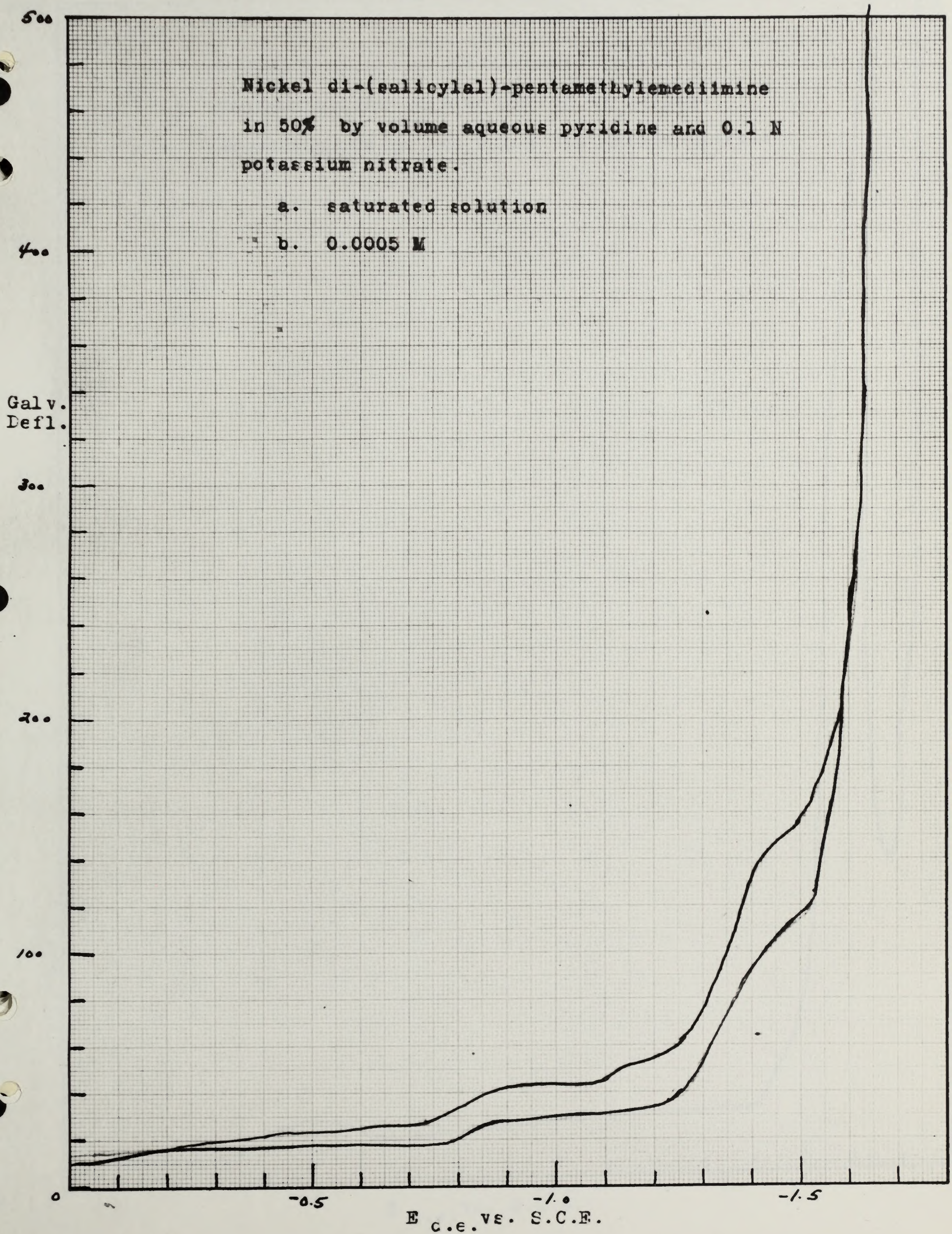
Fig. 17.



.0001 M nickel di-(salicylal)-ethylenediimine
in 50% by volume aqueous pyridine and 0.1 N
potassium nitrate. 1 ml. of 0.2% gelatin added
to 25 ml. of solution.
600
400
300
200
100
0
Galv.
Defl.
-0.5
-1.0
-1.5
E d.e. vs.S.C.E.

Fig. 18.

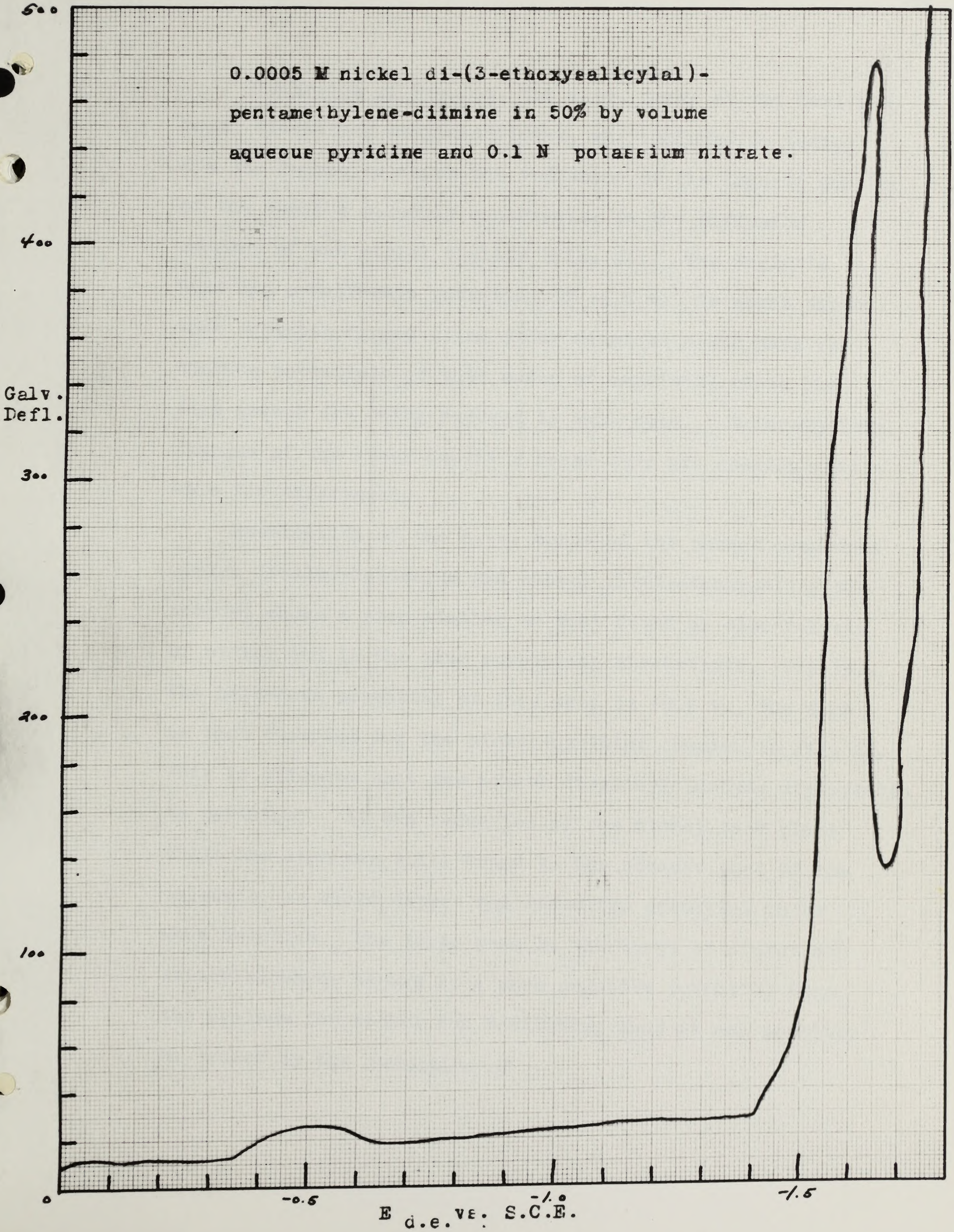


Nickel di-(salicylal)-pentamethylemediimine in 50% by volume aqueous pyridine and 0.1 N potassium nitrate.

a. saturated solution

b. 0.0005 M

Fig. 19.



0.0005 M nickel di-(3-ethoxysalicylal)-pentamethylene-diimine in 50% by volume aqueous pyridine and 0.1 N potassium nitrate.

<u>Discussion of Results</u>. The c.-v. curve of the Schiff's base, disalicyal-ethylenediimine, was included to indicate the degree to which the reduction of the organic portion of the chelate molecule contributes to the diffusion current of the nickel chelate (Fig. 13). The Schiff's base had a half-wave potential of -1.4 v. We might expect that chelates formed using other diamines would have reduction potentials of this order of magnitude since the same groupe are being reduced in each case. Unfortunately, samples of the other Schiff's bases were not readily available for experiment.

Examination of the c.-v. curve of the parent compounds nickel disalicylaldehyde and nickel di-(3-ethoxysalicylaldehyde) shows a step similar to that found on electrolysis of nickel ion in the same supporting electrolyte, (Fig.14). The half-wave potential of this step is -0.9 v., the same as that observed for the nickel-pyridine complex in Fig. 12. This is evidence that the nickel disalicylaldehyde dissociates in pyridine. If the reduction of the nickel took place while the atom was still bound to the organic part of the molecule, we would expect the reduction potential to be more negative. The large peak in the curve of nickel disalicylaldehyde occurs at a more negative potential than the maximum for nickel ion indicating that it may possibly be caused by the reduction of

a group in the organic portion of the molecule. Since there is no peak in the Schiff's base, we are led to believe that the maximum is due to the reduction of a group not present in the disalicylal-ethylene diimine. In the nickel disalicylaldehyde the aldehyde group is free but in the disalicylal-ethylenediimine this group has become an imine group.

The curves for nickel di-(salicylaldimine) and nickel di(3-ethoxysalicylaldimine) are quite similar (Fig. 15). The nickel step occurs here also but is diminished in amplitude compared to the same step in nickel disalicylaldehyde where it is over twice as high. This could be interpreted to mean that in the nickel di-(salicylaldimine) the nickel is more closely bound than in the parent compound, making the concentration of free nickel ion less in solution. A second step whose half-wave potential is -1.15 v. appears to be a reduced version of the peak occurring in the curve of nickel disalicylaldehyde. Here is evidence to disprove the theory that the peak in Fig. 14 is due to the reduction of the aldehyde group. Quite possibly the nickel still held in the undissociated molecule is being reduced at this more negative potential in conformity with what we would expect. If this is true, we can postulate an equilibrium between the nickel chelate and nickel-pyridine complex ions and chelate ions. If the step with the half-wave potential of -1.15 v. is due to the reduction of nickel in the molecule then the equilibrium is slow compared to the rate of reduction. The ratio of the undissociated mole-

cules to the dissociated is roughly two to one since the height of the second step is twice that of the first. The organic portion of the molecule is then reduced at a still more negative potential in an irreversible fashion.

The curve of nickel di-(salicylalmethylimine) is rather different in that it exhibits a high maximum which is reduced sufficiently, however, by the addition of gelatin as a suppressor to allow comparison of the two imine derivatives. Comparison of Fig. 15b with Fig. 16b shows that they are nearly identical with the exception of the large peak at - 1.4 v. This peak could be ascribed to the reduction of the methylimine group since it occurs nowhere else in the curves studied.

Examination of the polarogram of nickel di-(salicylal) ethylene-diimine (Fig. 17) shows that linking the two halves of the complex together effects a considerable change in its stability. Consisting of a single step whose half-wave potential is -1.55 v., the curve is markedly different from those discussed above. Noticeably absent is the step previously postulated as arising from the reduction of the nickel ion. Also no step occurs that can be attributed to the nickel retained in the complex. The single step has a half-wave potential of -1.55 but it is difficult to know to what group to attribute this step since consideration of the disalicylalethylenediimine compound showed that the organic portion of the molecule was reduced at -1.4 v. The small slope

of the curve would seem to point to the nickel ion as the part of the complex being reduced since the reduction of the Schiff's base gives a curve with a much larger slope. Possibly the reduction of the organic part of this chelate is obscured by the sharp rise in the diffusion current brought about by the reduction of the potassium ion from the indifferent salt. While we cannot with any certainty state what factor is the cause of the single step in this curve, we can safely conclude that the linking together of the complex increases the stability of the nickel chelate sufficiently to prevent any dissociation of the type postulated for the chelates not linked in this fashion.

The next member of the series found to be soluble in the 50% by volume aqueous pyridine was the nickel di-(salicylal)-pentamethylenediimine whose c.-v. curve is reproduced in Fig. 18. Here the curve has a single step similar to that found for the ethylenediimine compound but the half-wave potential is - 1.37 v. vs. the saturated calomel electrode. Although this reduction potential is not as negative as that found for the nickel di-(salicylal)-ethylenediimine, the compounds are comparable in their stability. Examination of the polarogram of nickel di-(3-ethoxysalicylal)-pentamethylenediimine (Fig. 19) shows a remarkable difference. No adequate explanation can be offered for the existence of the large maximum appearing at - 1.6 v. The small hump appearing at 0.5 v. is also a new development. In all the compounds

previously discussed the ethoxy substituted ones did not differ in any respect in their polarographic behavior from that of the unsubstituted chelates.

CHAPTER IV

LIGHT ABSORPTION OF NICKEL CHELATES

I. EXPERIMENTAL

The data for the absorption spectra in this investigation were obtained using a Beckman spectrophotometer model DU. Using the tungsten lamp provided with the equipment it was possible to obtain data from 320 millimicrons to 1000 millimicrons. In actual practice the compounds did not absorb beyond 800 millicrons. The cells used to contain the solutions were one centimeter thick. If larger cells had been available, it would have been desirable to use them in obtaining data in the regions where light absorption is so low as to render the measurements inaccurate. Ordinarily use of a more concentrated solution would obviate this difficulty but the nickel chelates cannot be dissolved to such an extent.

The benzene used was of Baker's C.P. grade. The pyridine used initially was of Baker's C. P. grade. When the supply of this failed, it became necessary to recover the pyridine by drying over sodium hydroxide and then fractionating through a column having the equivalent of thirty plates. This yielded pyridine having a boiling point the same as that reported in the literature.

In most cases two concentrations have been used in obtaining the data, although in the case of the disalicylalethylenediimine compounds three different concentrations were

used. It will be found that a few of the curves are incomplete in the regions of longer wave-lengths because of the lack of solubility of these compounds in the particular solvent. The extinction curves for nickel di-(3-ethoxysalicylal)hexamethylenediimine and nickel di-(3-ethoxysalicylal)-decamethylenediimine could not be obtained in benzene (or in alcohol since they are insoluble).

The data from which the extinction curves have been plotted are tabulated in the appendix. The concentrations used for the different compounds are listed also.

II. RESULTS

The following tables list the maxima found for each compound in benzene and pyridine. The value for the logarithim of the extinction coefficient is also noted. The compounds are grouped according to their similarities.

The quantity denoted as E is referred to as ε, the molecular extinction coefficient, by Brode (19).

It was calculated from $E = k d \frac{c}{M}$

where k = specific extinction (determined experimentally)

c = concentration in g/l

d = cell thickness

M = molecular weight of compound

BENZENE SOLUTIONS

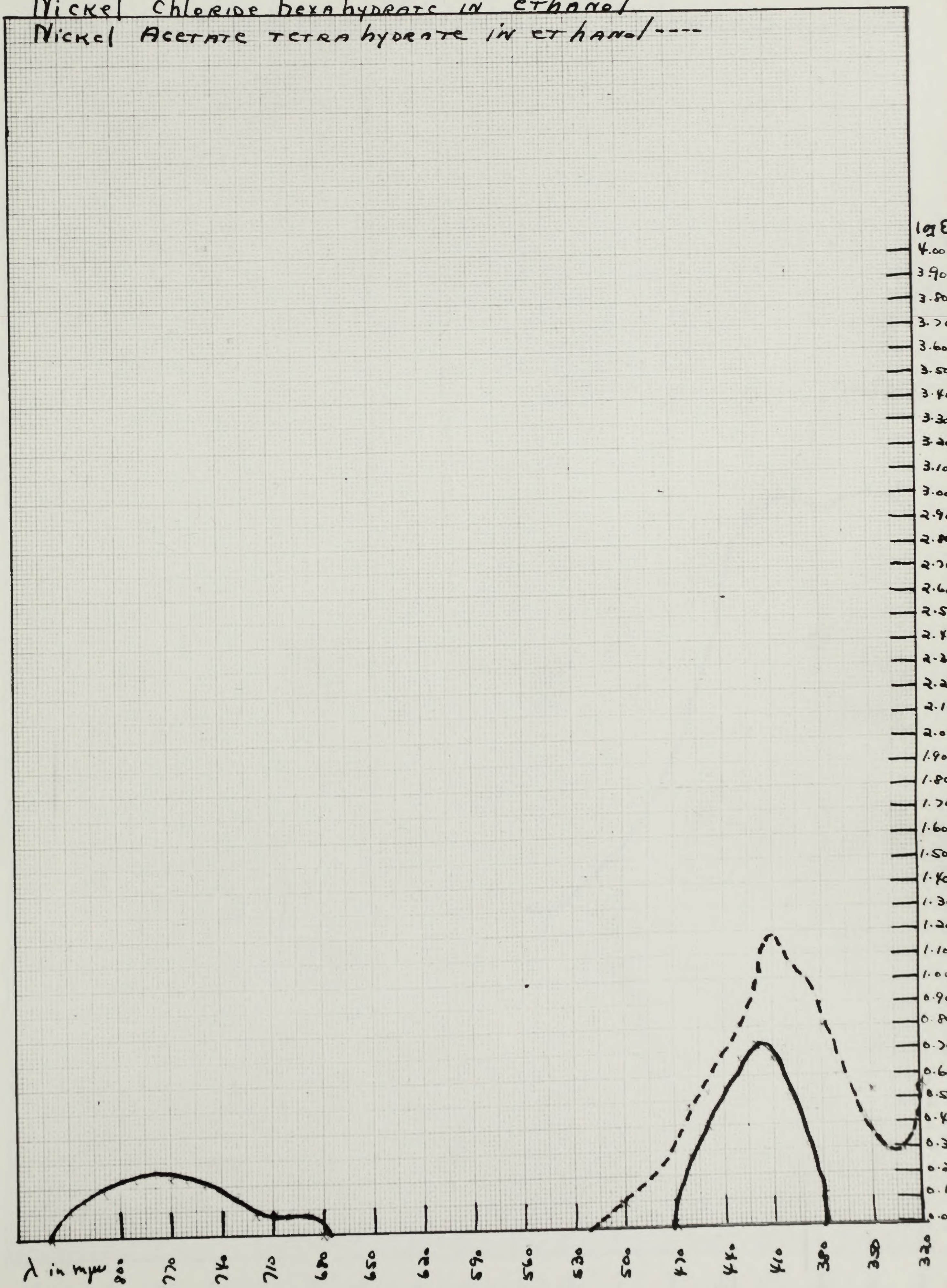
Fig. No.	Compound	Maxima	Log E
20	nickel chloride*	420	0.74
		780	0.26
43	di-(salicylal)-ethylenediimine*	320	3.90
		410	2.88
41	di-(salicylal)-ethylenediimine*	320	3.98
		425	1.40
44	di-(3-ethoxysalicylal)-ethylenidiimine	335	3.64
		430	1.80
21	nickel di-(3-ethoxysalicylaldehyde)*	350	3.08
		400	3.06
24	nickel di-(3-ethoxysalicylal)-ethylenediimine	335	3.94
		425	3.86
		560	2.24
23	nickel di-(3-ethoxysalicylaldimine)	340	4.02
		420	3.54
		560	1.96
22	nickel di-(3-ethoxysalicylalmethylimine)	335	3.92
		420	3.56
		620	1.96
46	nickel di-(3-ethoxysalicylal)-heptamethylenediimine	365	3.79
		430	3.76
		620	1.96
28	nickel di-(3-ethoxysalicylal)-nonamethylenediimine	335	3.68
		420	3.34
		630	1.92
26	nickel di-(3-ethoxysalicylal)-trimethylenediimine	365	3.82
		430	3.70
25	nickel di-(3-ethoxysalicylal)-trimethylenediimine dihydrate	360	3.76
		430	3.65
27	nickel di-(3-ethoxysalicylal)-pentamethylenediimine	360	3.88
		430	3.70

*These compounds insoluble in benzene. Data determined for alcohol solution.

PYRIDINE SOLUTIONS

Fig. No.	Compound	Maxima	log E
29	nickel chloride hexahydrate	320 390	2.10 0.96
30	nickel chloride dihydrate	320 380 650	2.40 1.04 0.70
42	di-(salicylal)-ethylenediimine	320 410	3.82 2.00
45	di-(3-ethoxysalicylal)-ethylenediimine	340 425	3.66 2.26
34	nickel di-(3-ethoxysalicylal)-ethylenediimine	350 410 570	3.90 3.93 2.12
33	nickel di-(3-ethoxysalicylaldimine)	340 390 570	3.74 3.80 1.66
35	nickel di-(3-ethoxysalicylal)-trimethylenediimine	330 390 560	3.26 3.92 1.34
36	nickel di-(3-ethoxysalicylal)-pentamethylenediimine	380 575	3.70 1.80
38	nickel di-(3-ethoxysalicylal)-heptamethylenediimine	390 545	3.94 1.60
31	nickel di-(3-ethoxysalicylaldehyde)	350 410 635	3.54 3.60 0.90
32	nickel di-(3-ethoxysalicylalmethylimine)	340 390 610	3.52 3.72 1.00
37	nickel di-(3 ethoxysalicylal)-hexamethylenediimine	390 600	3.84 0.96
39	nickel di-(3-ethoxysalicylal)-nonamethylenediimine	330 415 605	3.60 3.64 0.96
40	nickel di-(3-ethoxysalicylal)-decamethylenediimine	340 390 610	3.42 3.44 1.08

Fig. 20



Nickel chloride hexahydrate in ethanol

Nickel acetate tetrahydrate in ethanol ----

Fig. 21

Nickel di-3-Ethoxysalicylaldehyde in Ethanol

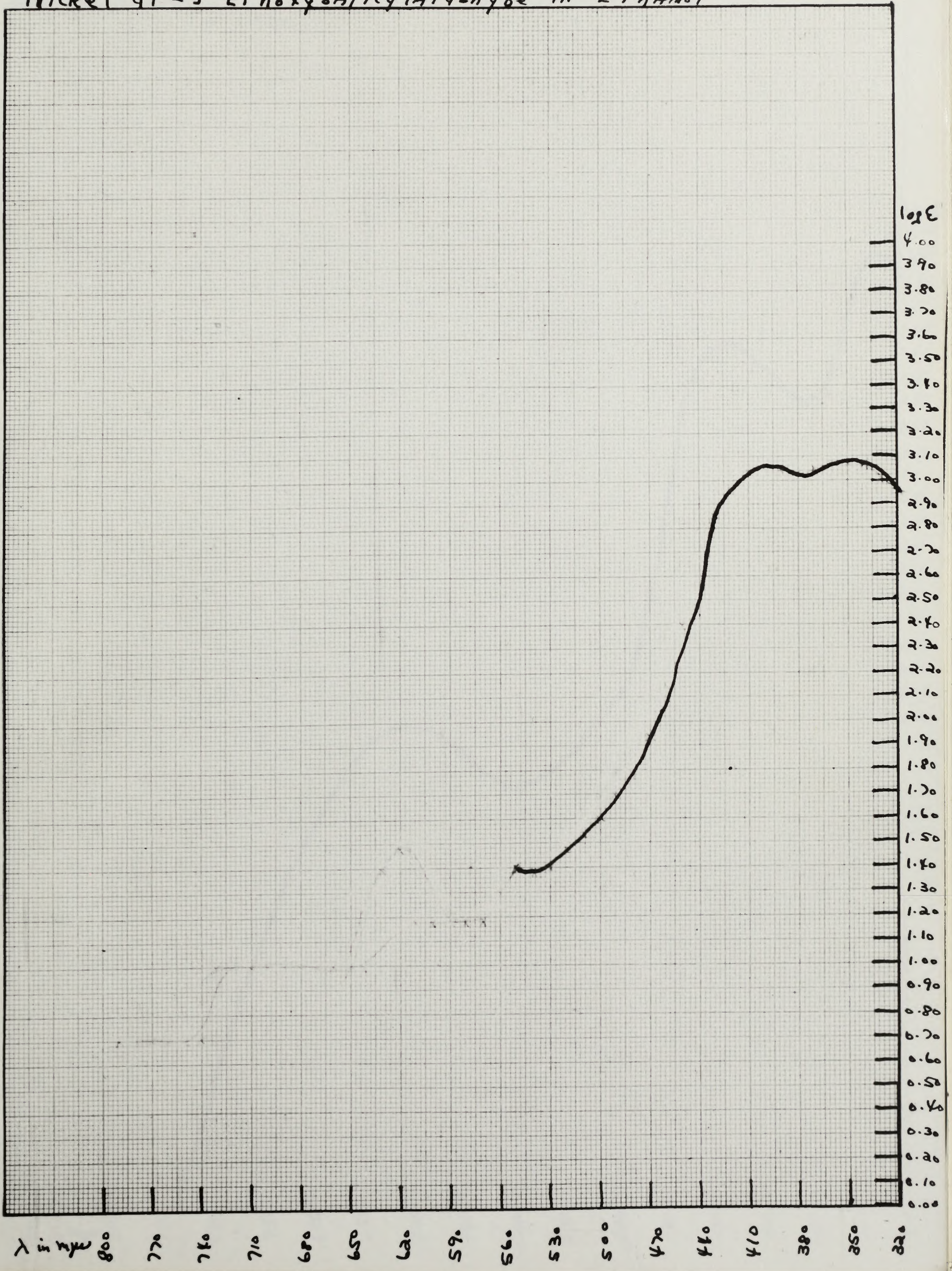


Fig. 22

Nickel di-(3-ethoxysalicylalmethylimine) in Benzene

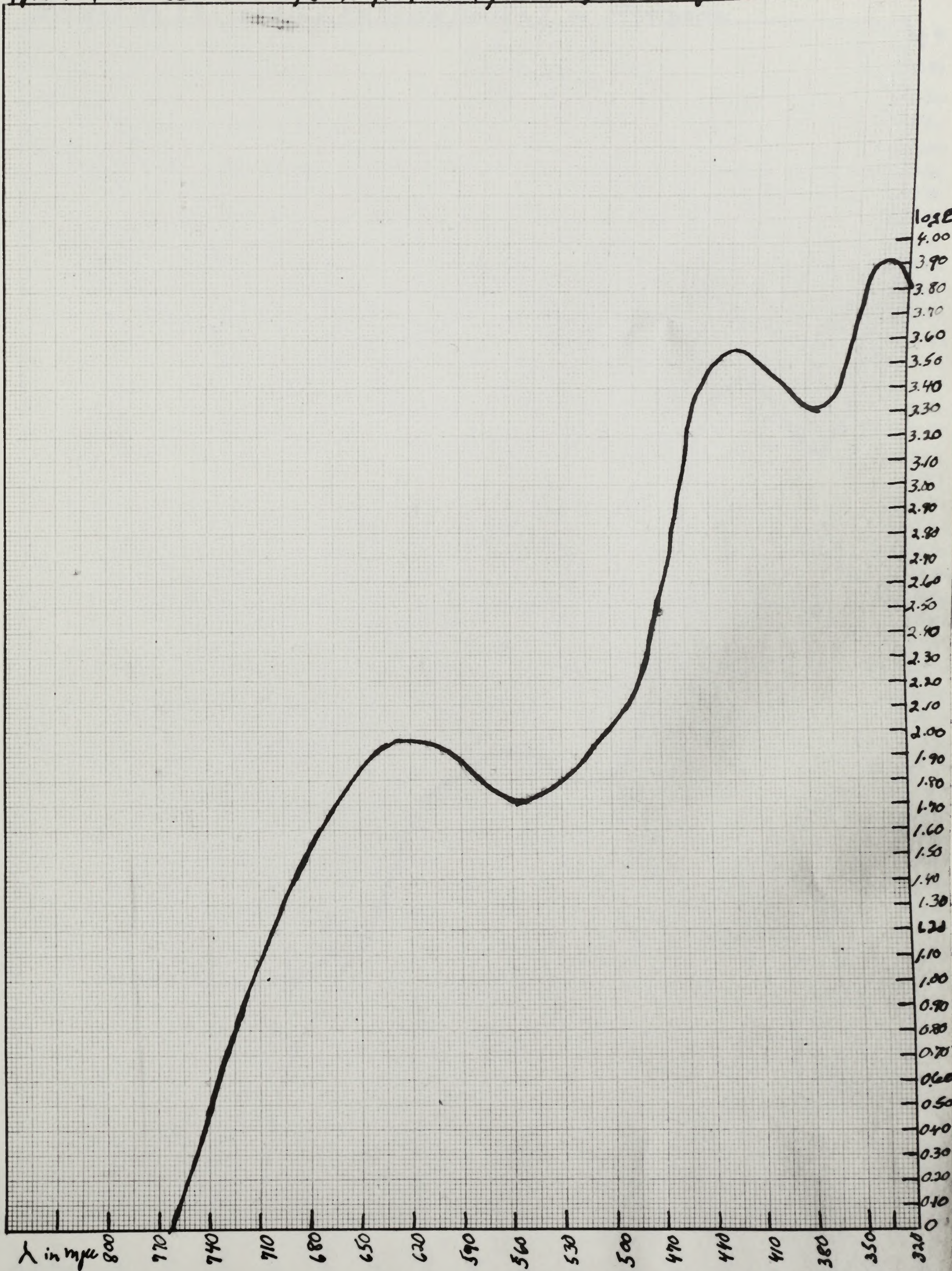


Fig. 23

Nickel di (3- ethoxy salicylaldimine) in Benzene

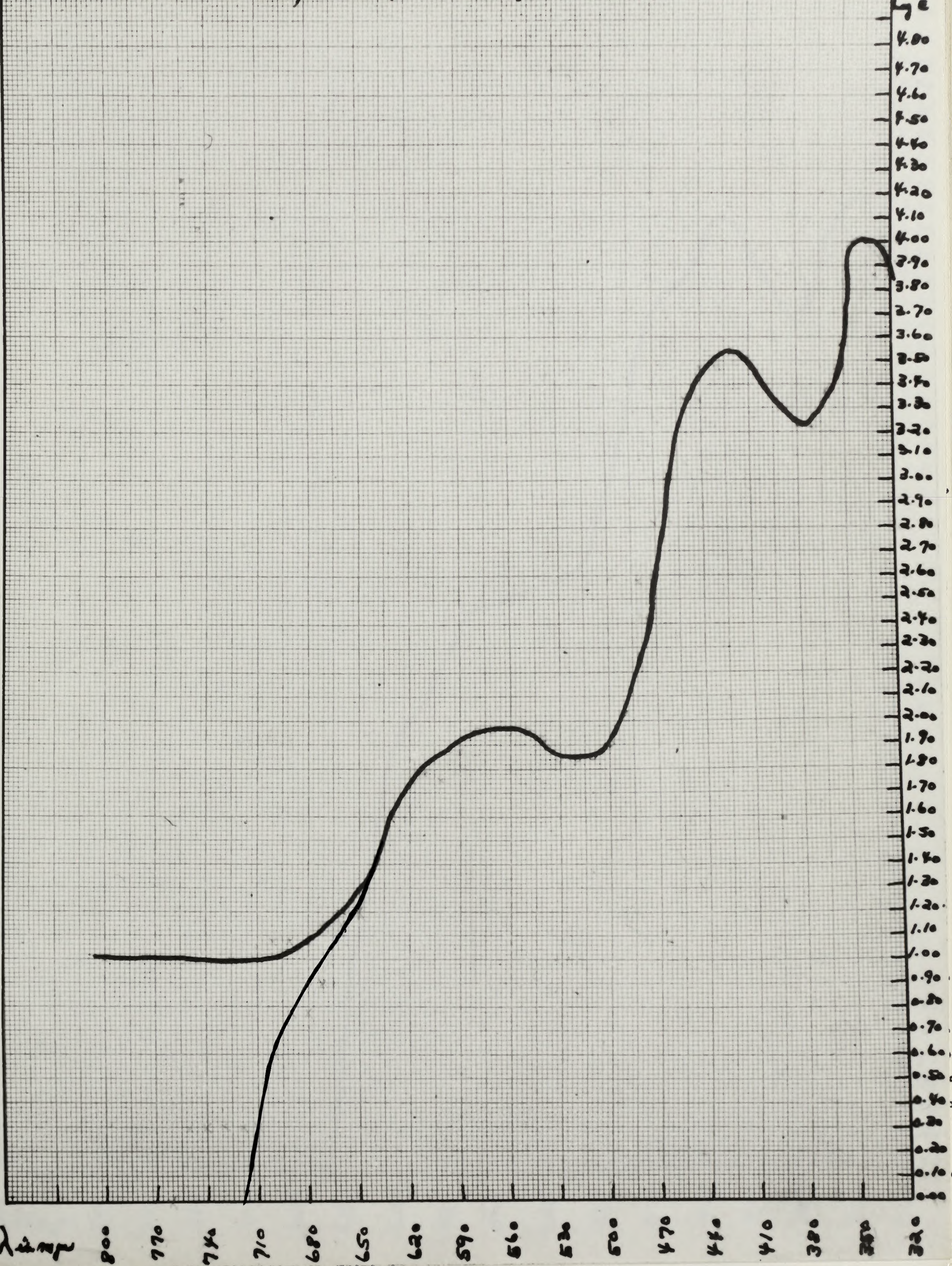


Fig. 24

Nickel di-(3-ethoxy salicylal) ethylene Diimine in Benzene

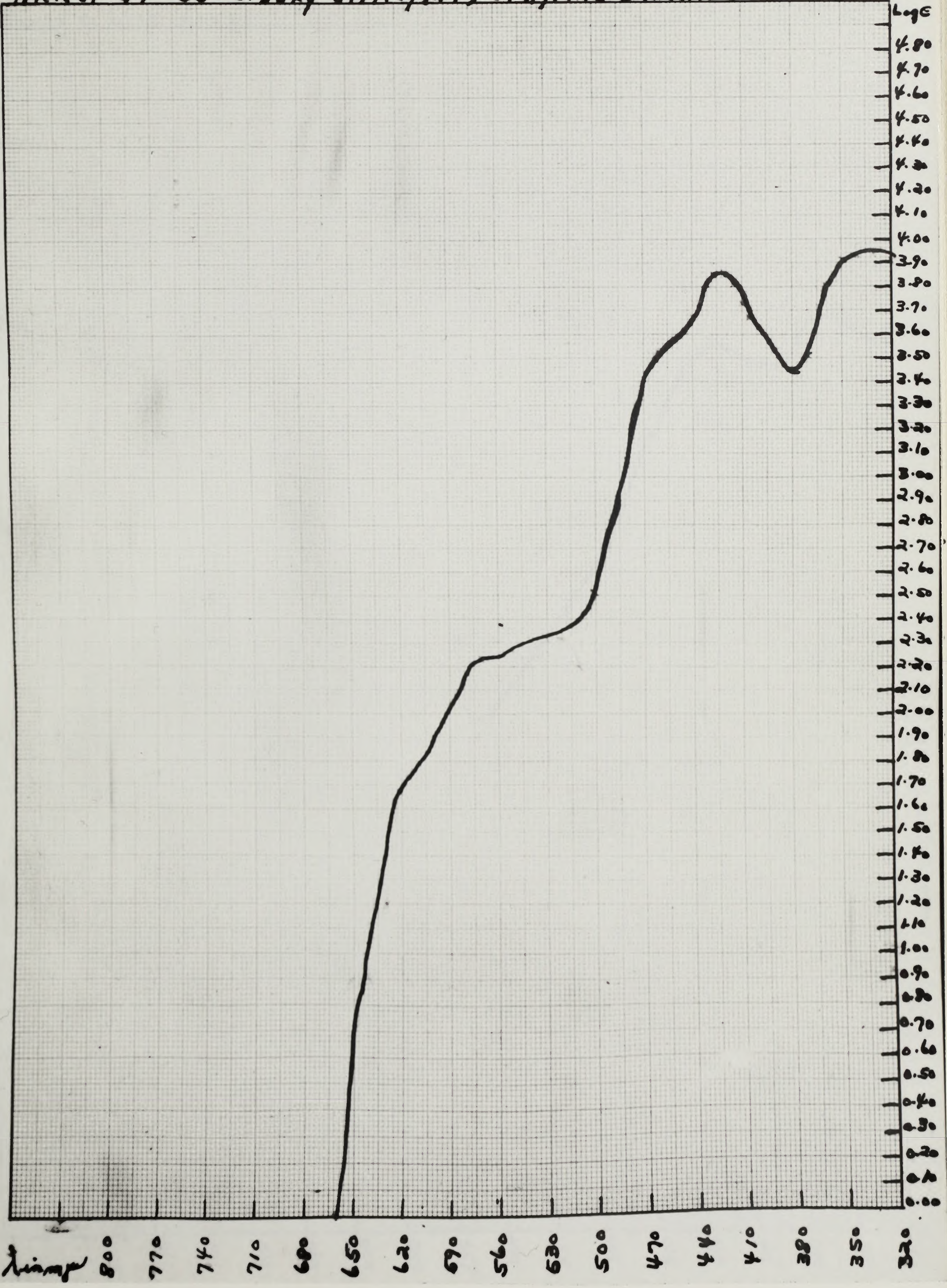


Fig. 25

Nickel di (3-Ethoxysalicylal)-Trimethylenediimine dihydrate in Benzene

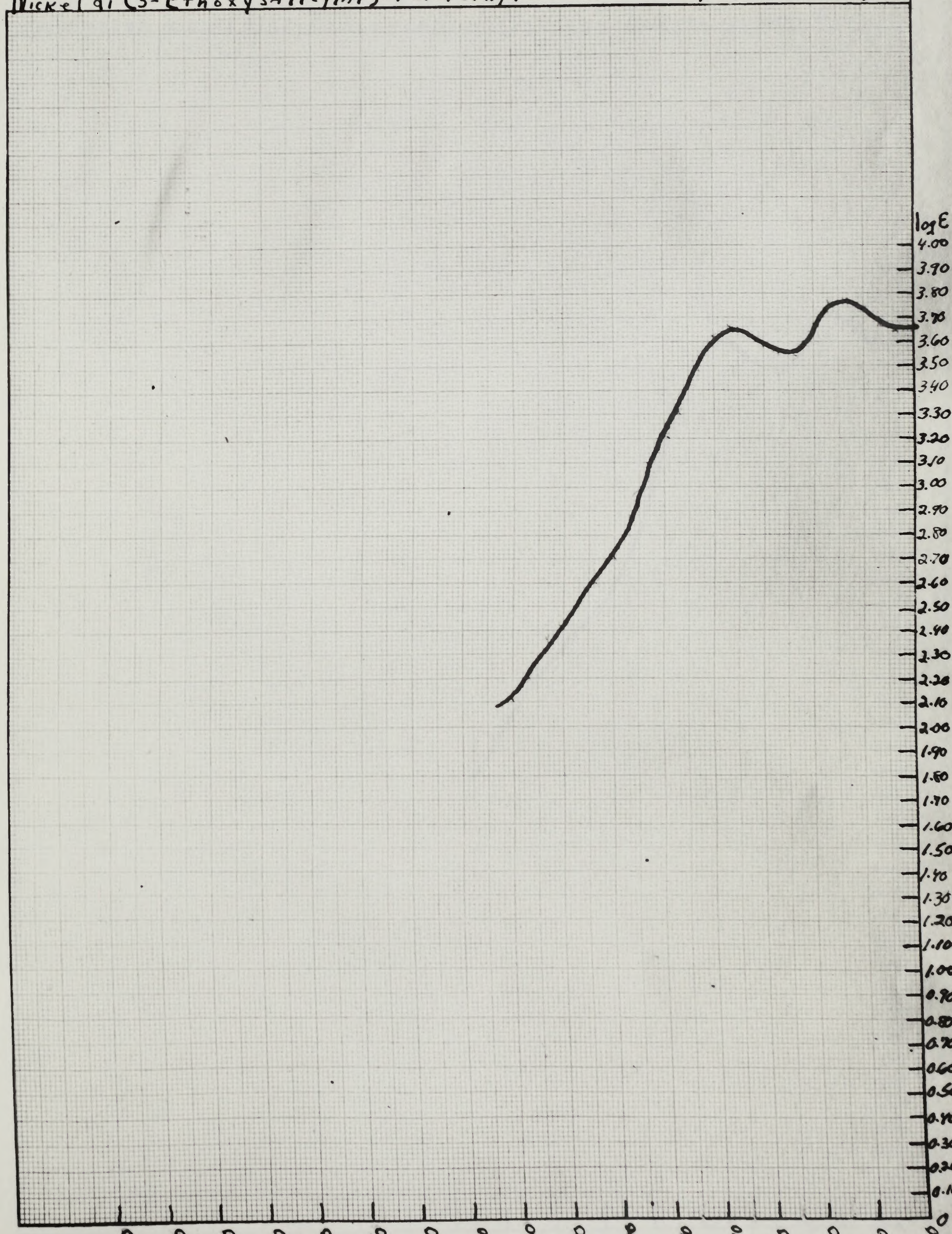


Fig. 26

Anhydrous nickel di(3-Ethoxysalicylal)-trimethylenediimine in Benzene

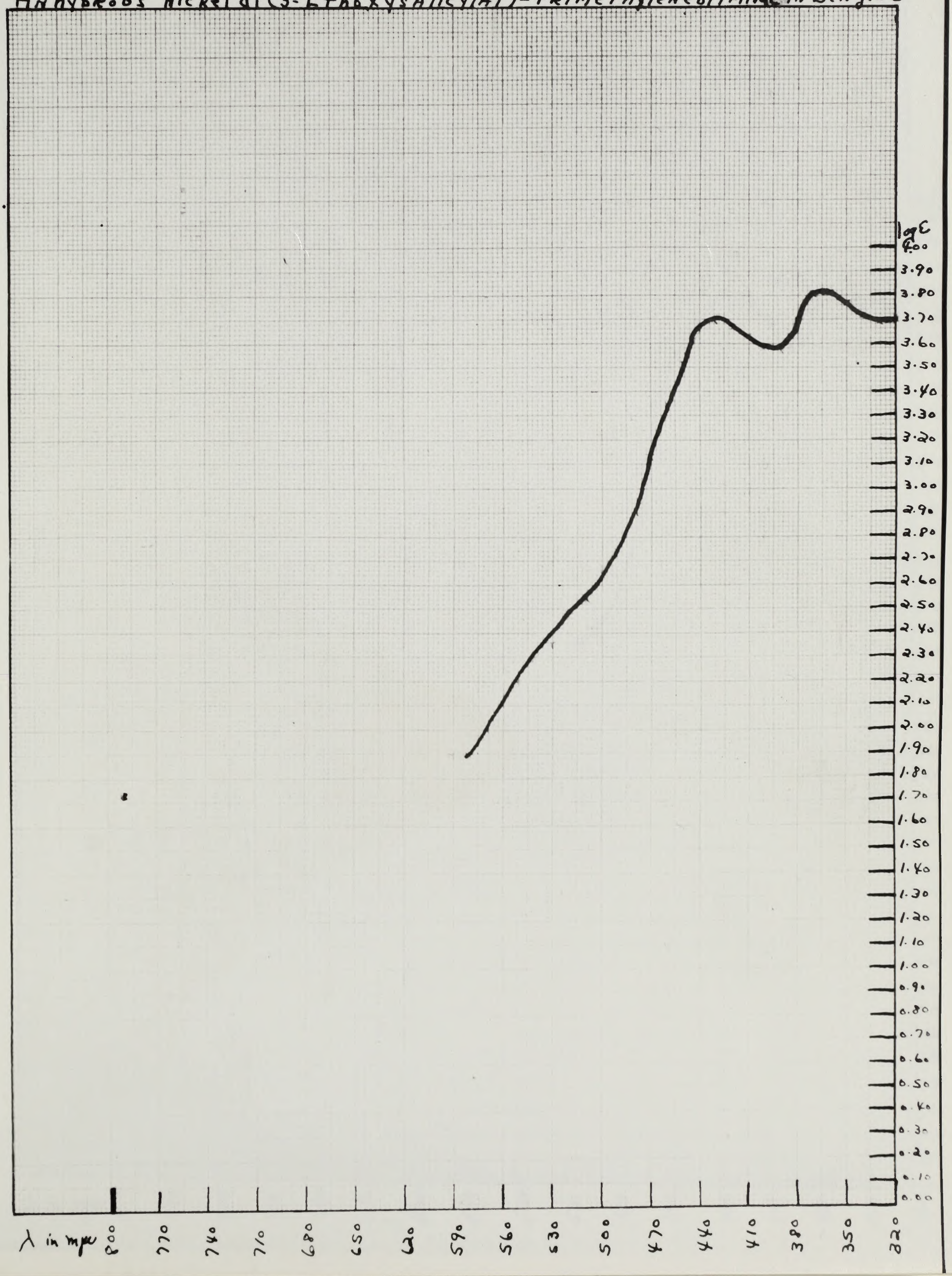


Fig. 27

Nickel di(3-Ethoxysalicylal)-pentamethylenediimine in Benzene

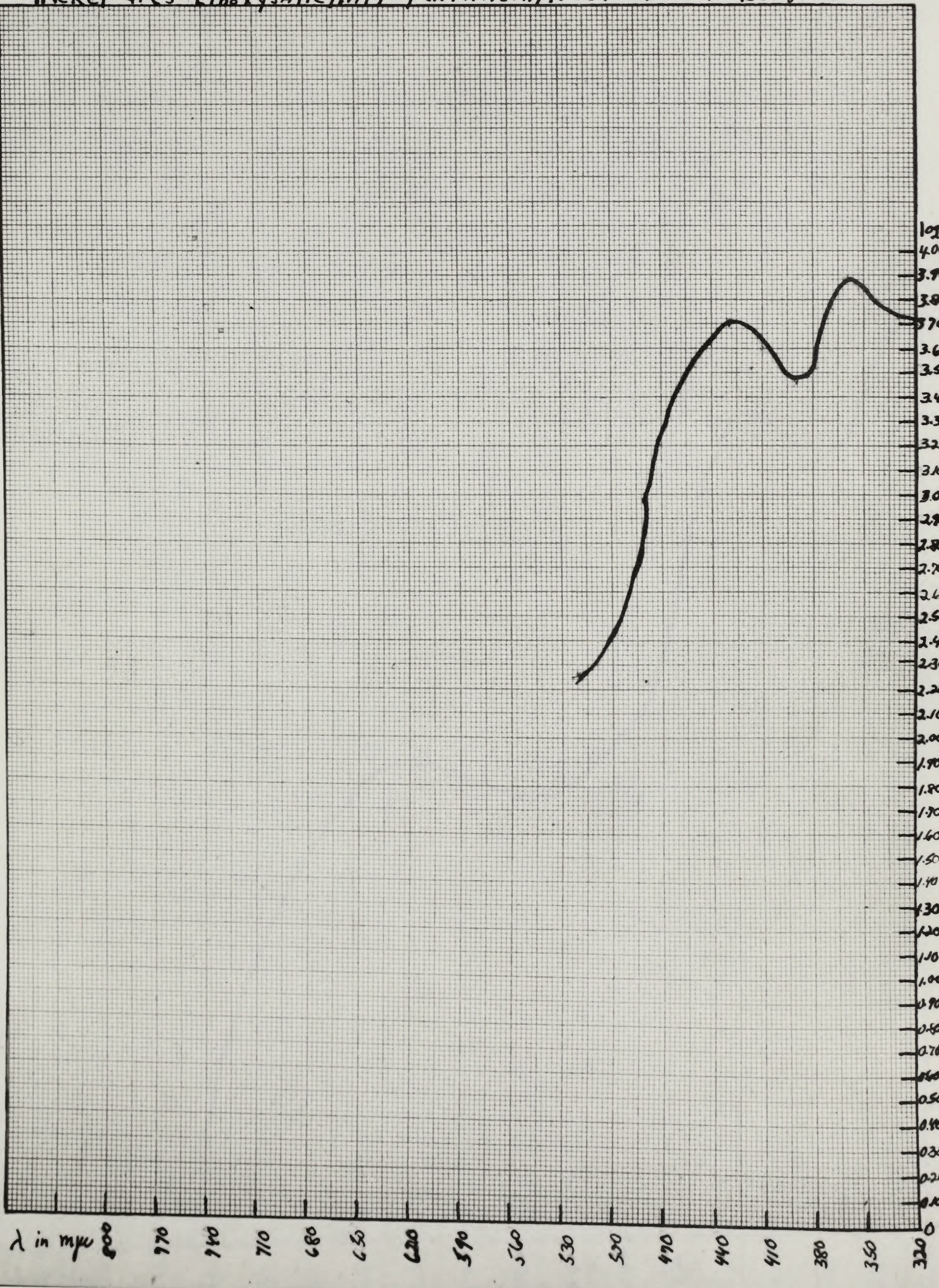


Fig. 28

Nickel di(3-Ethoxysalicylal)-nonamethylenediimine in Benzene

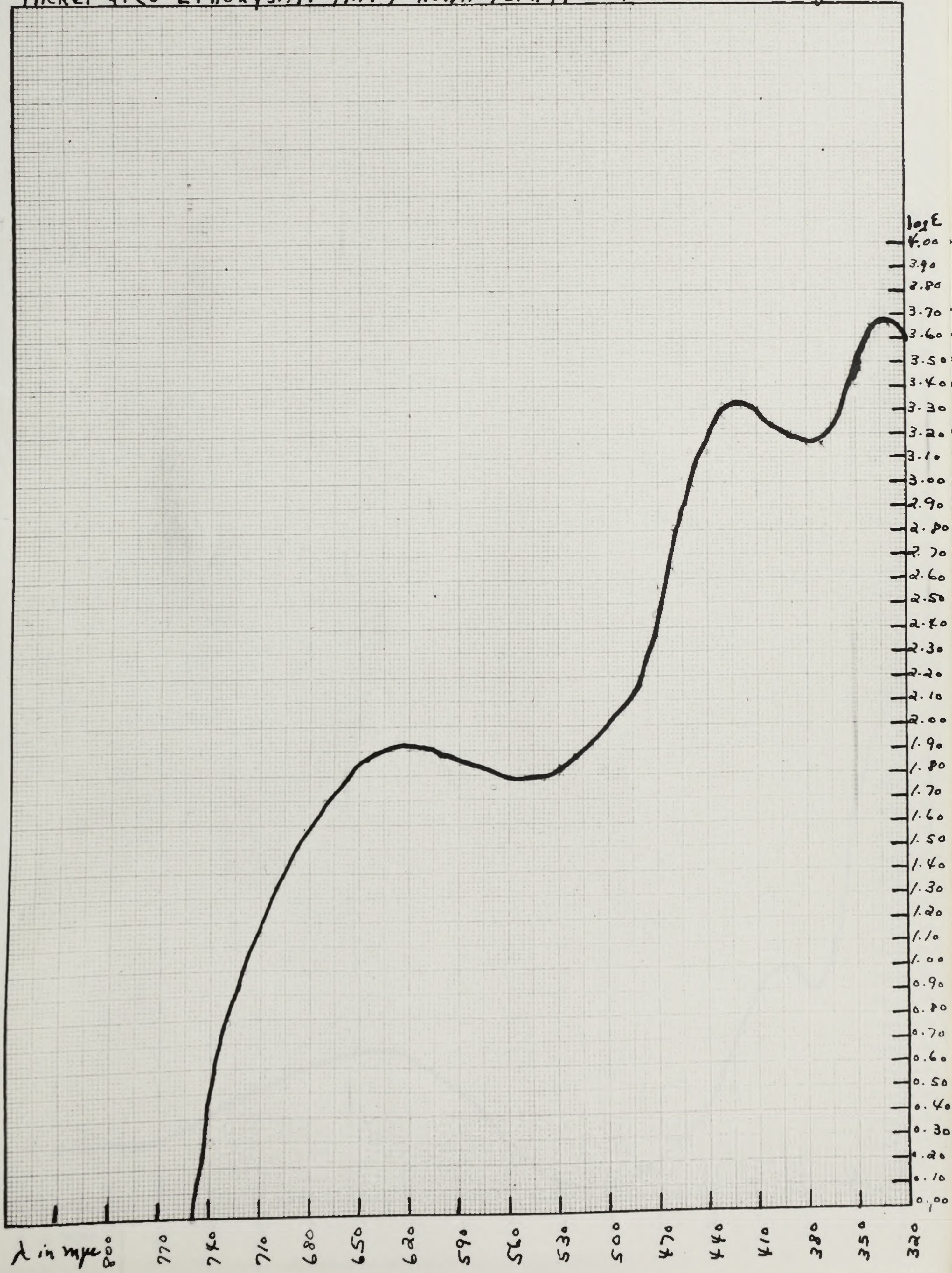


Fig. 29

Nickel chloride Hexahydrate in Pyridine

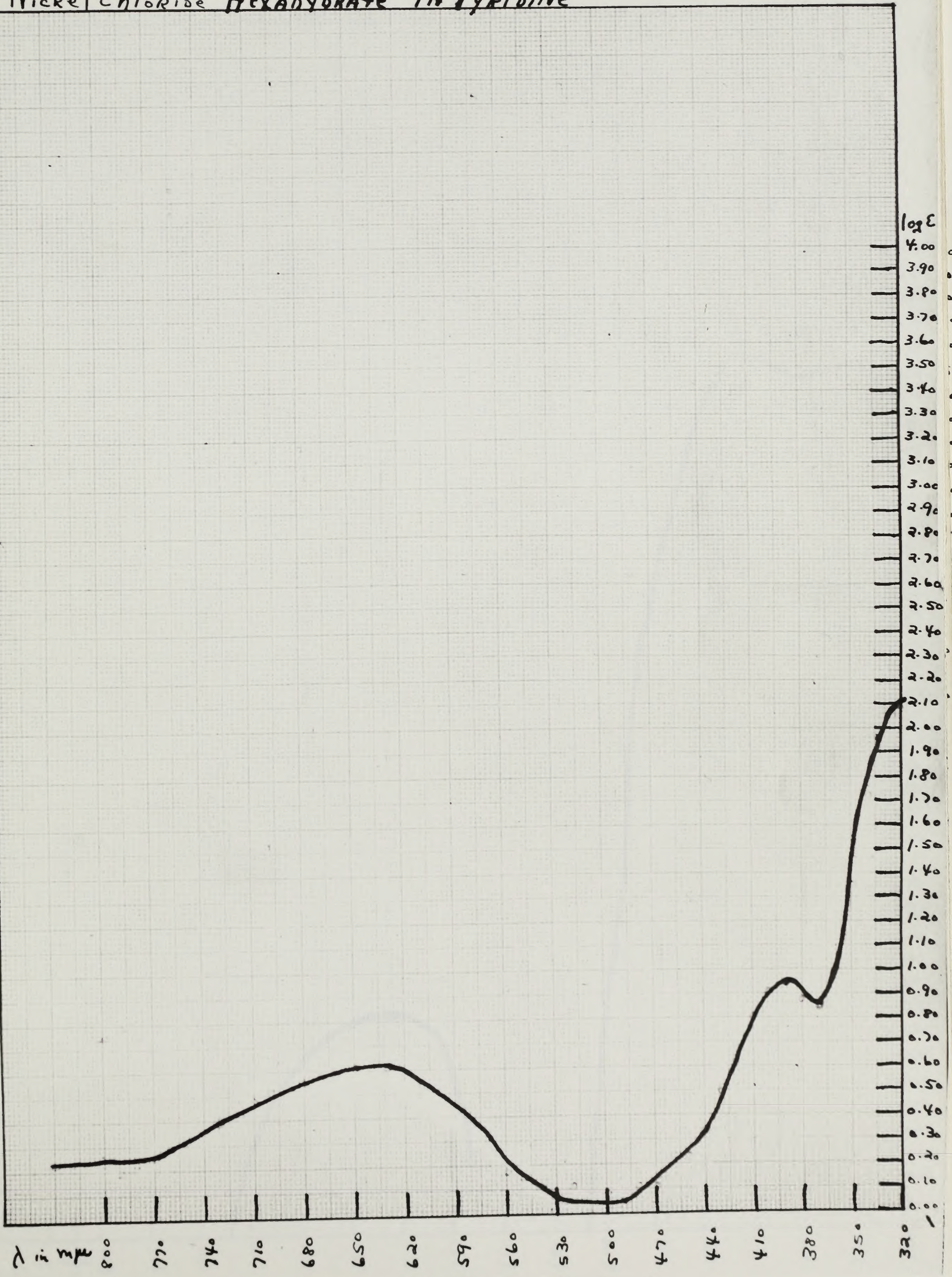


Fig. 31

Nickel di-3-ethoxysalicylaldehyde in Pyridine

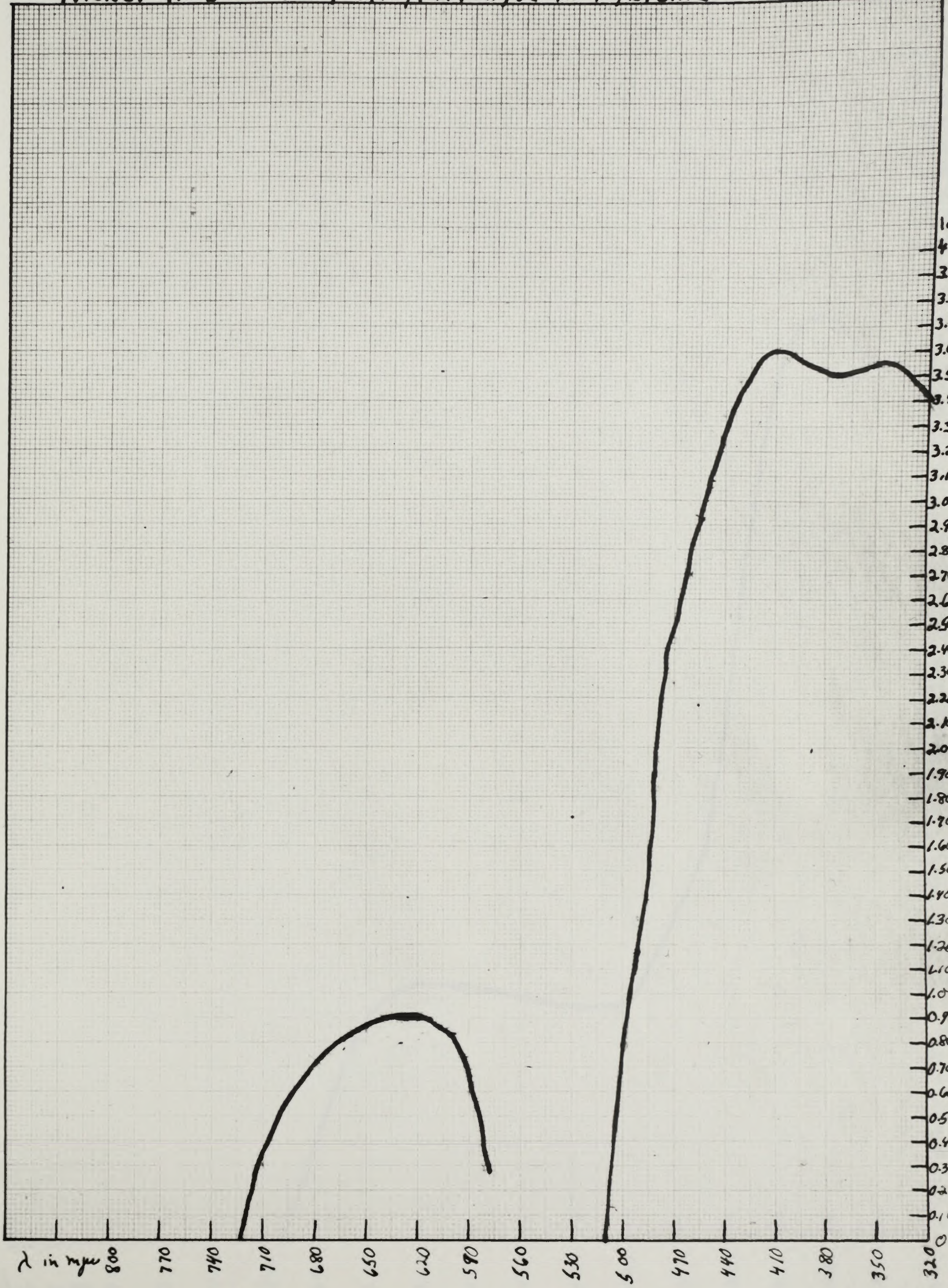


Fig. 32

Nickel di-(3-Ethoxysalicylalmethylimine) in Pyridine

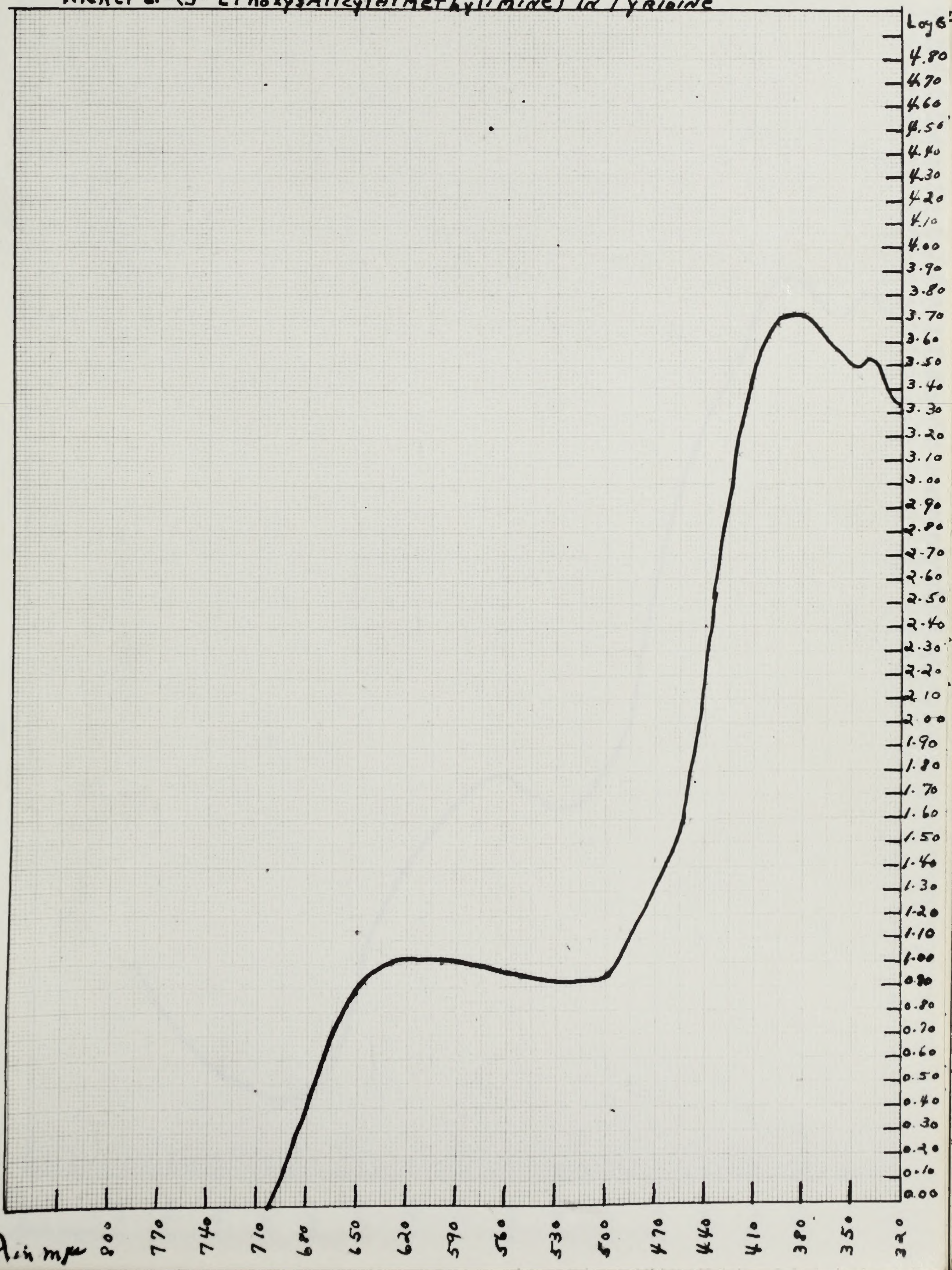


Fig. 33

Nickel di-(3-ethoxysalicylalimine) in Pyridine

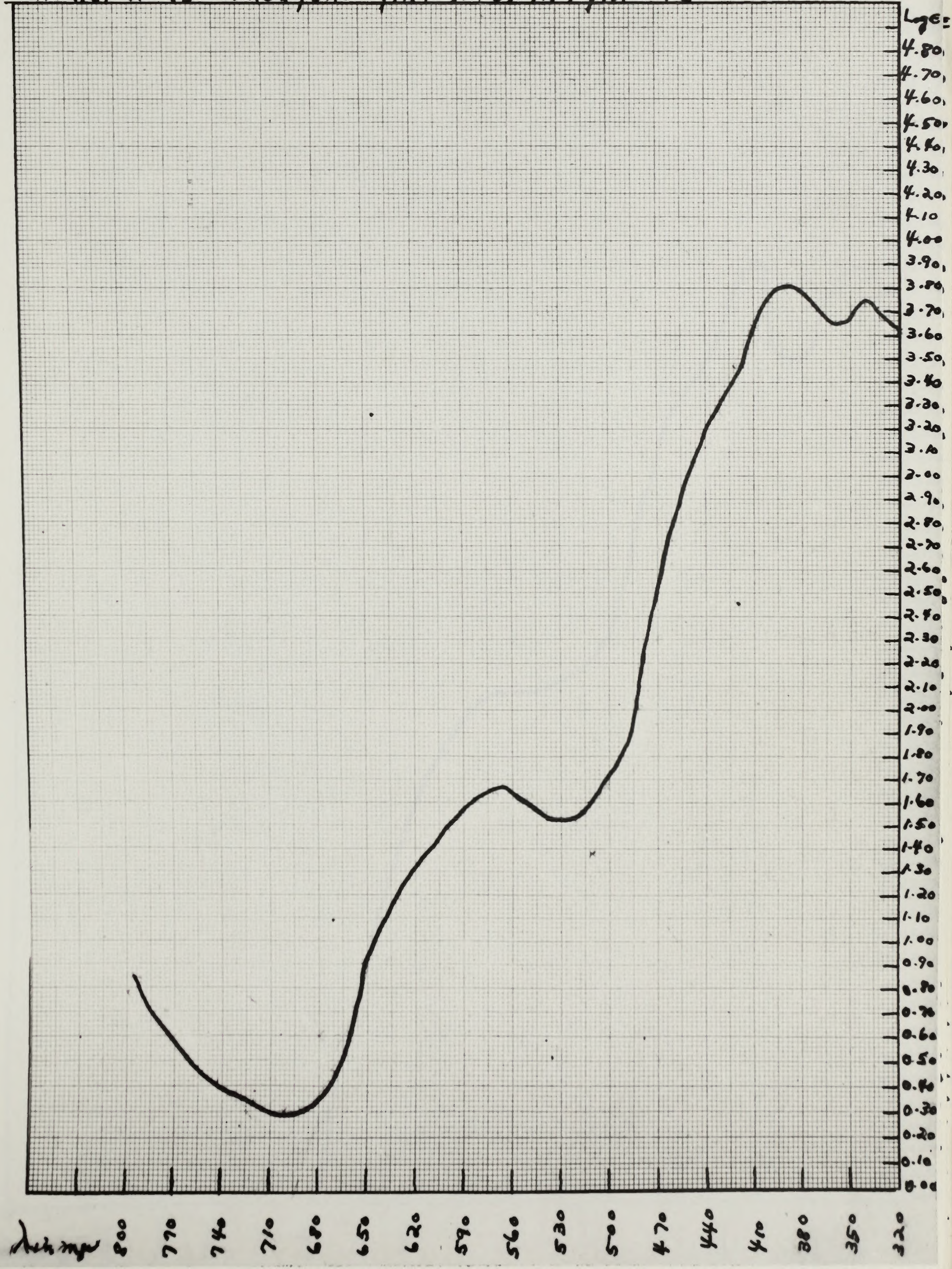


Fig. 34

Nickel di (3-Ethoxysalicylal)-ethylenediimine in Pyridine

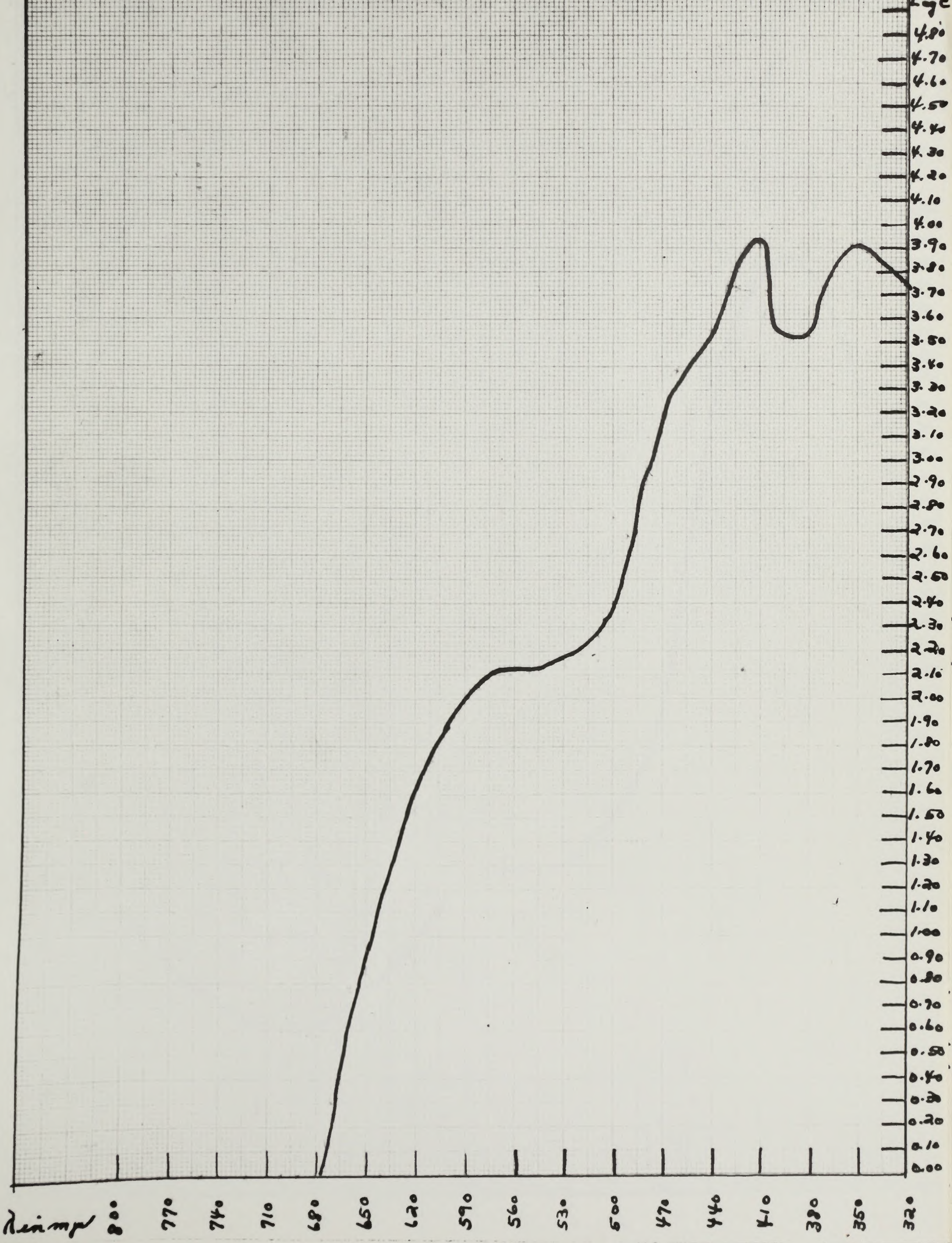


Fig. 35

Nickel di-(3-ethoxysalicylal) trimethylenediimine in Pyridine

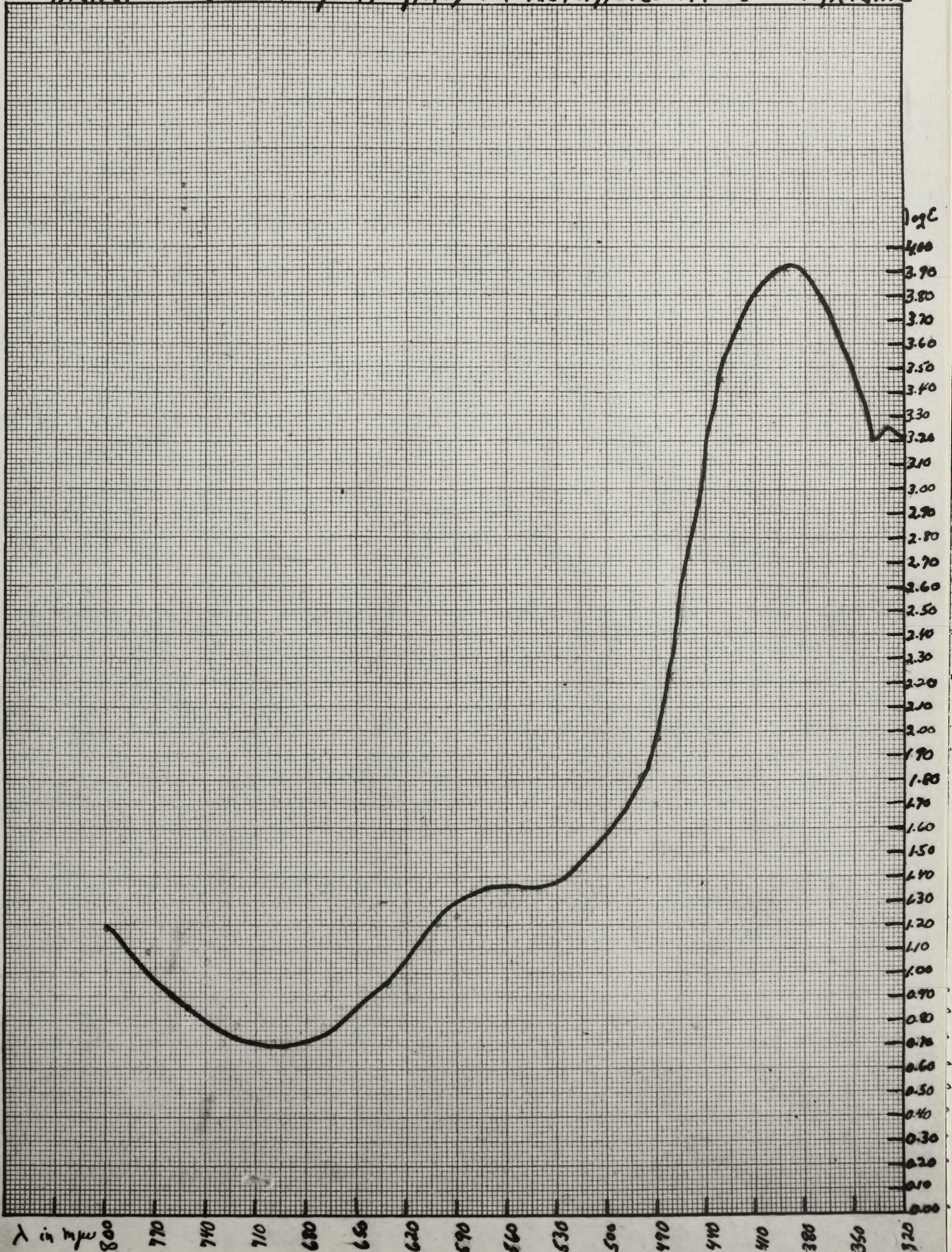


Fig. 36

Nickel di-(3-ethoxysalicylal) pentamethylene Diimine in Pyridine

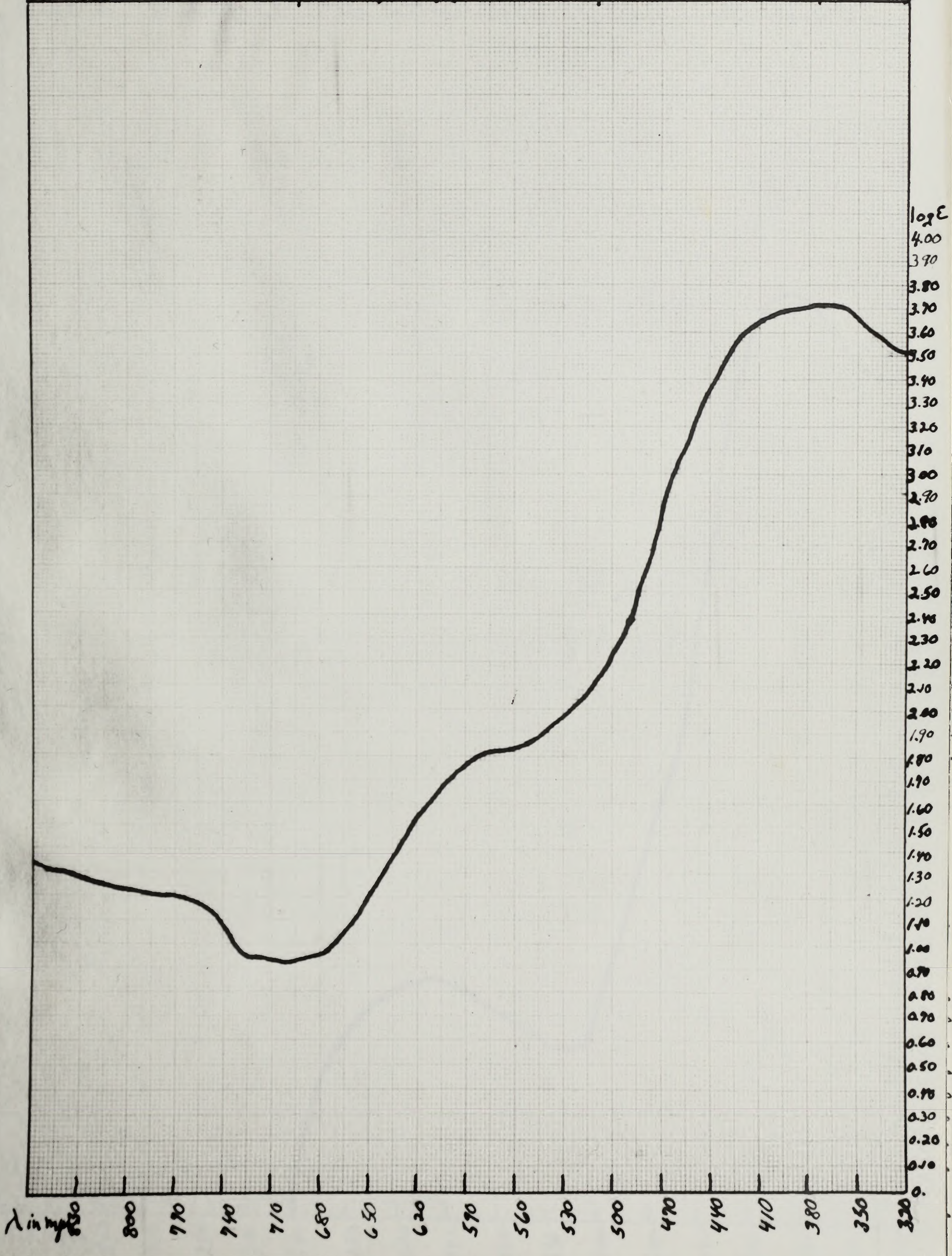


Fig. 37

Nickel di-(3-Ethoxysalicylal)-hexamethylenediimine in Pyridine

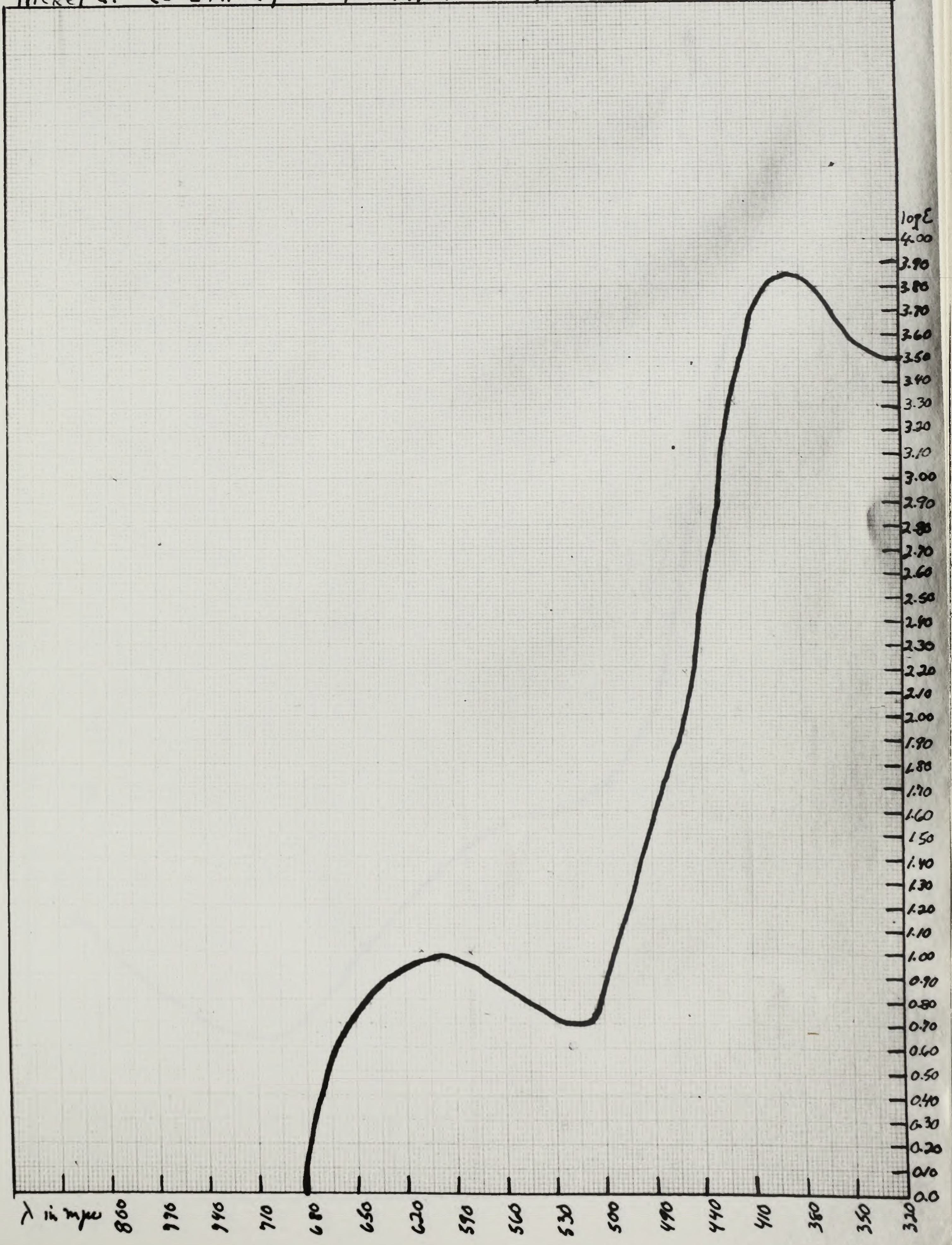


Fig. 38

Nickel di(3-Ethoxysalicylal)-heptamethylenediimine in Pyridine

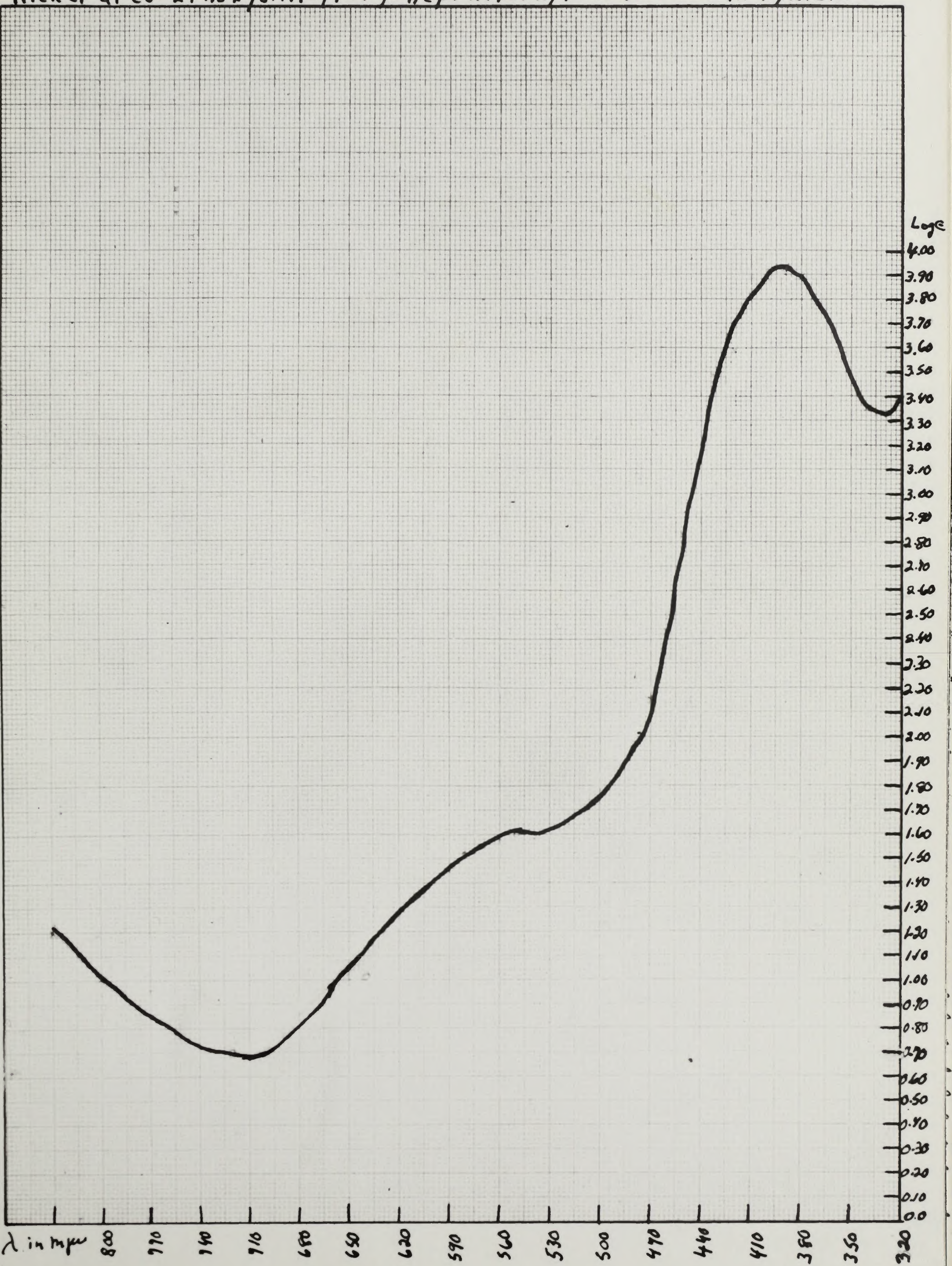


Fig. 39

Nickel di(3-Ethoxysalicylal)-nonamethylenediimine in Pyridine

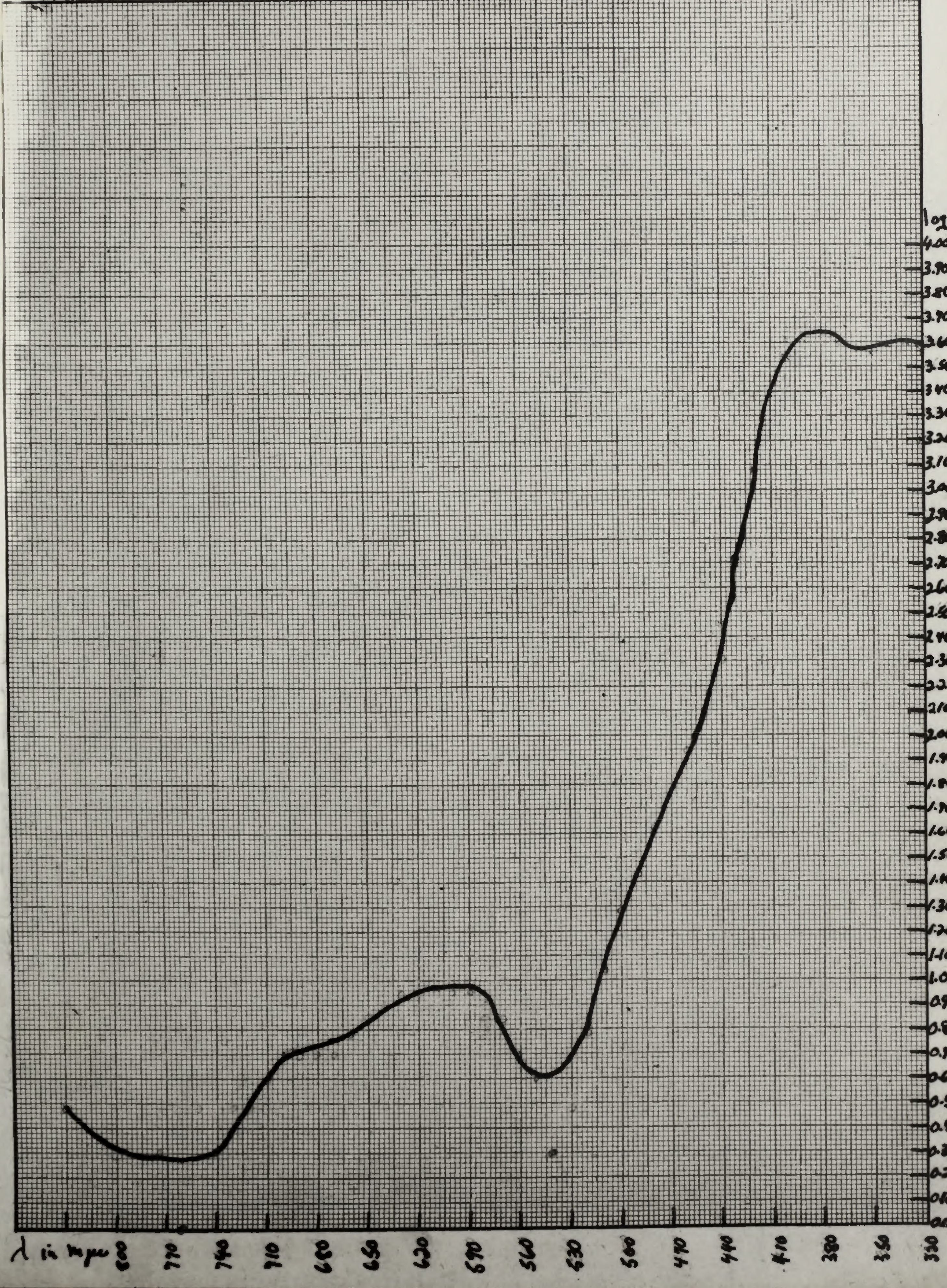


Fig. 40

Nickel di(3-Ethoxysalicylal)-decamethylenediimine in Pyridine

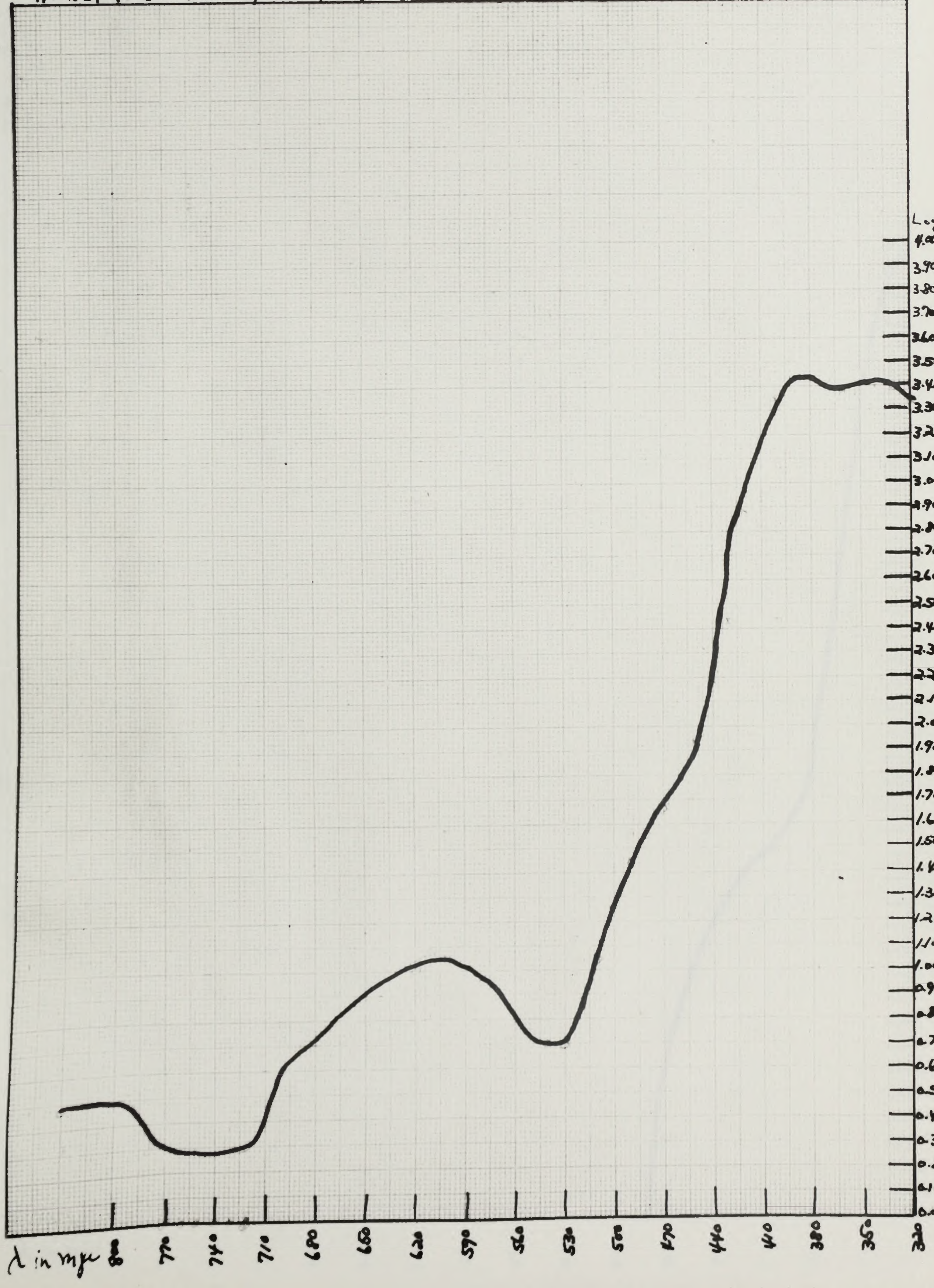


Fig. 41

Disalicylal-ethylenediimine in benzene

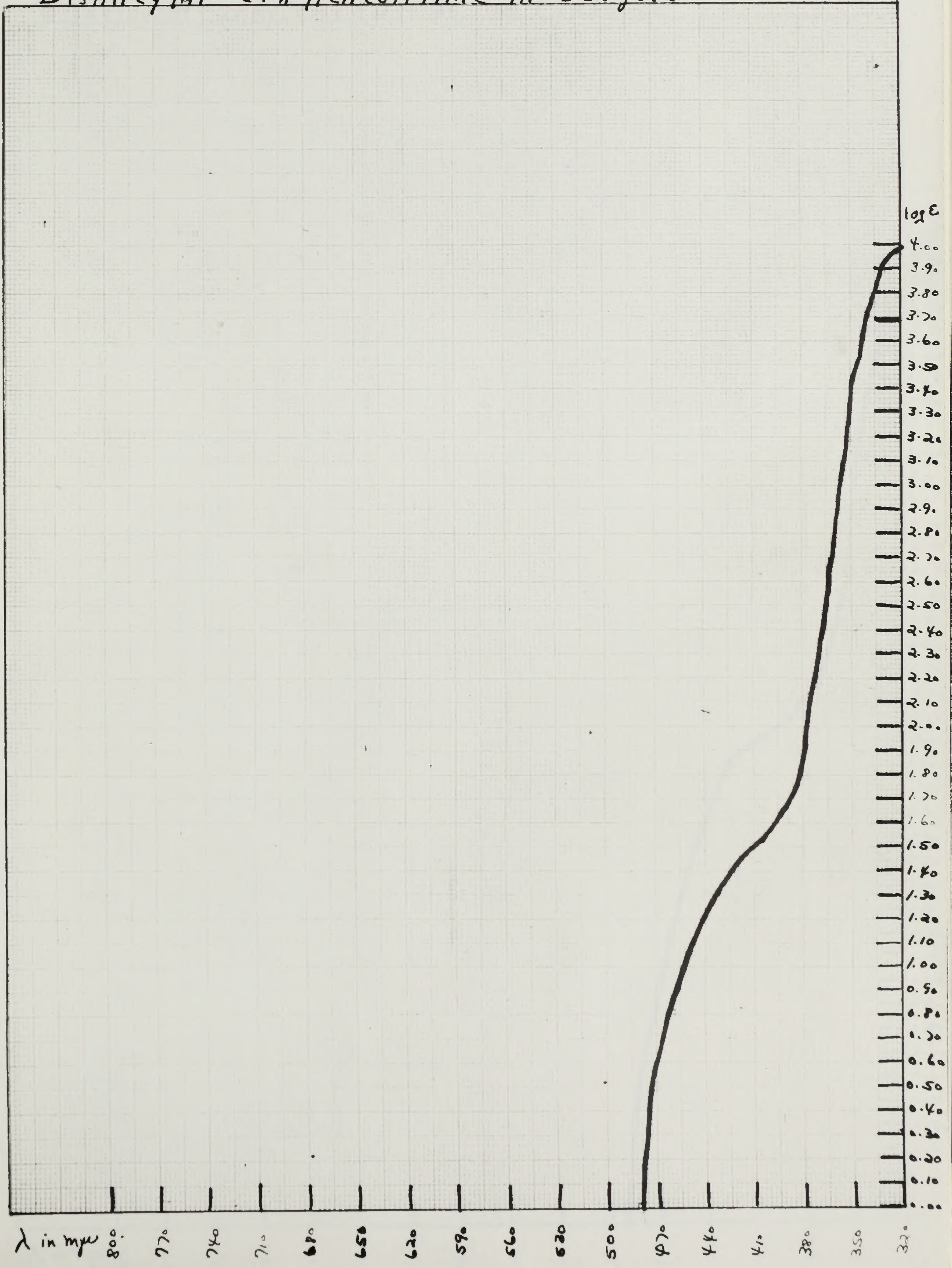


Fig. 42

Disalicylal-ethylenediimine in Pyridine

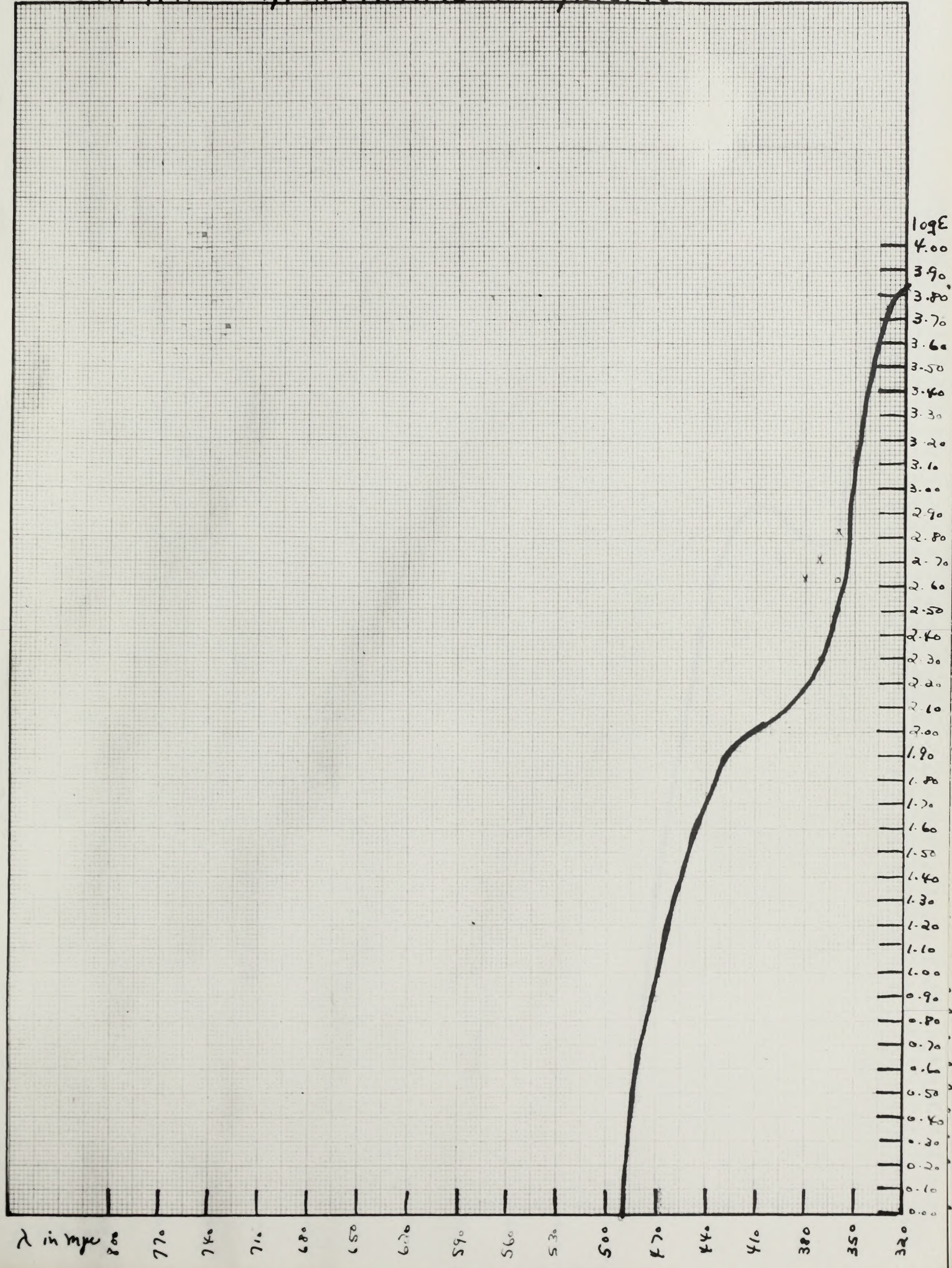


Fig. 43

Disalicylal-ethylenediimine in ethanol

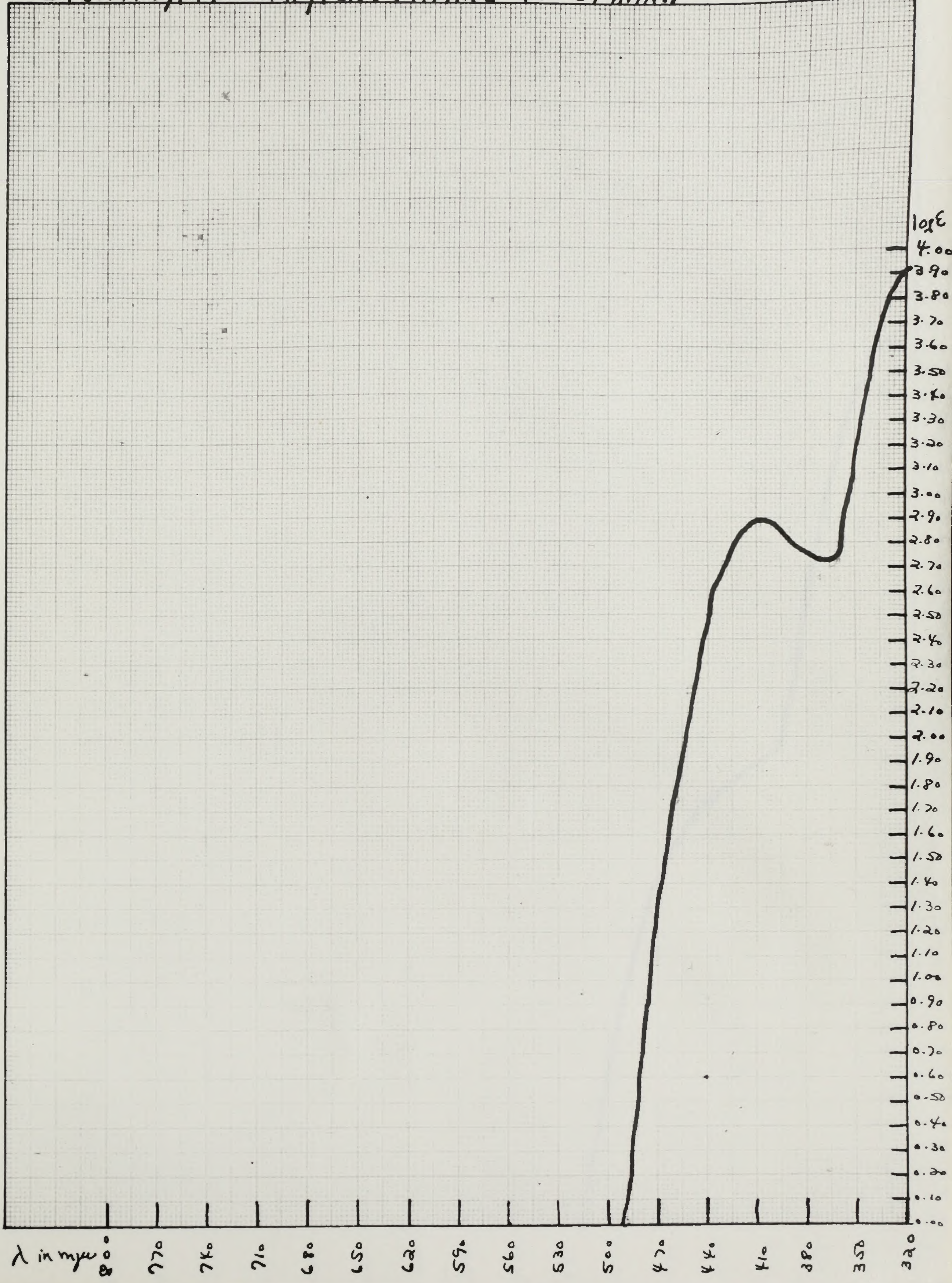


Fig. 44

Di-(3-ethoxysalicylal)-ethylenediimine in Benzene

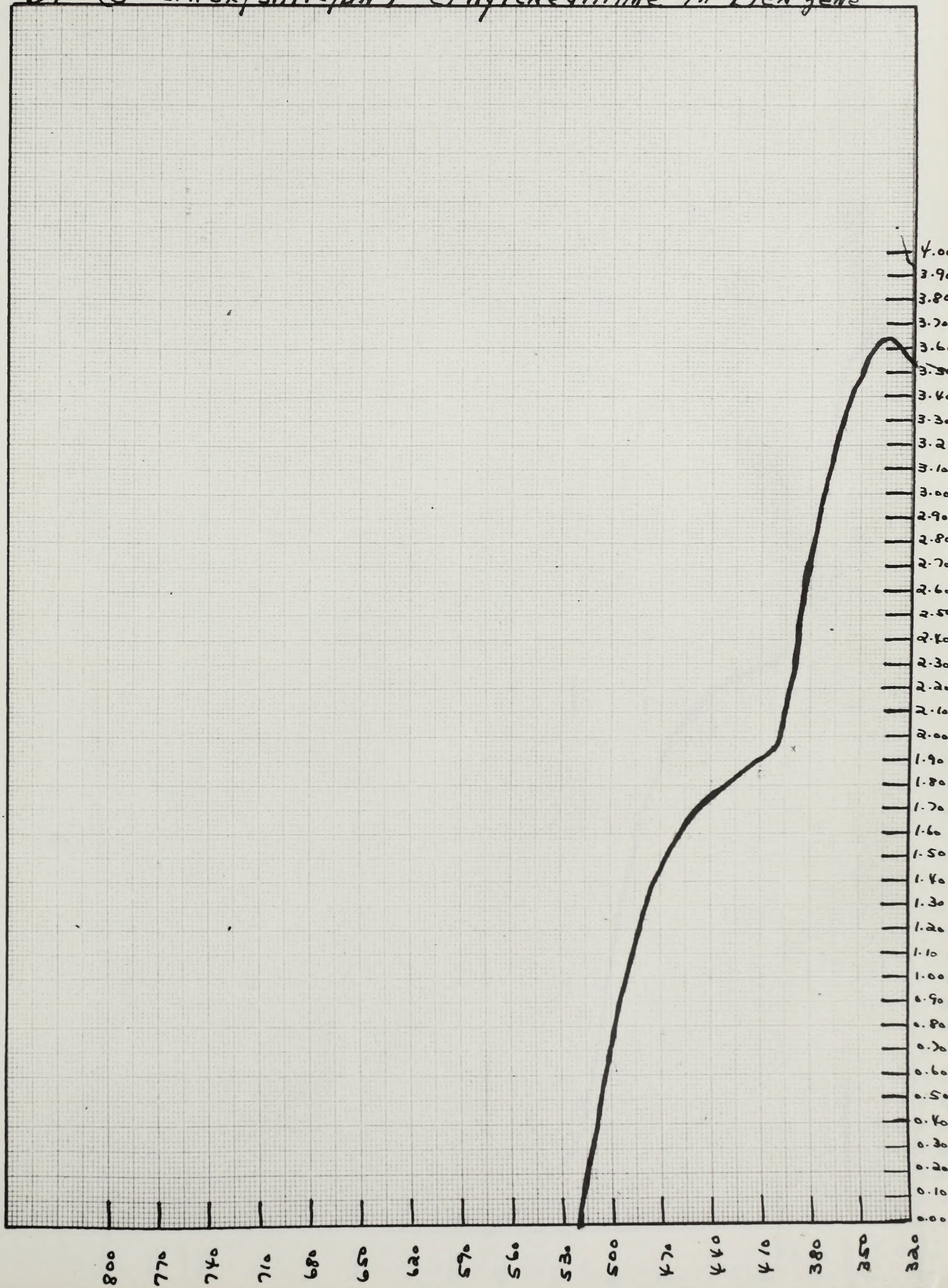


Fig. 45

Di-(3-ethoxysalicylal)-ethylenediimine in Pyridine

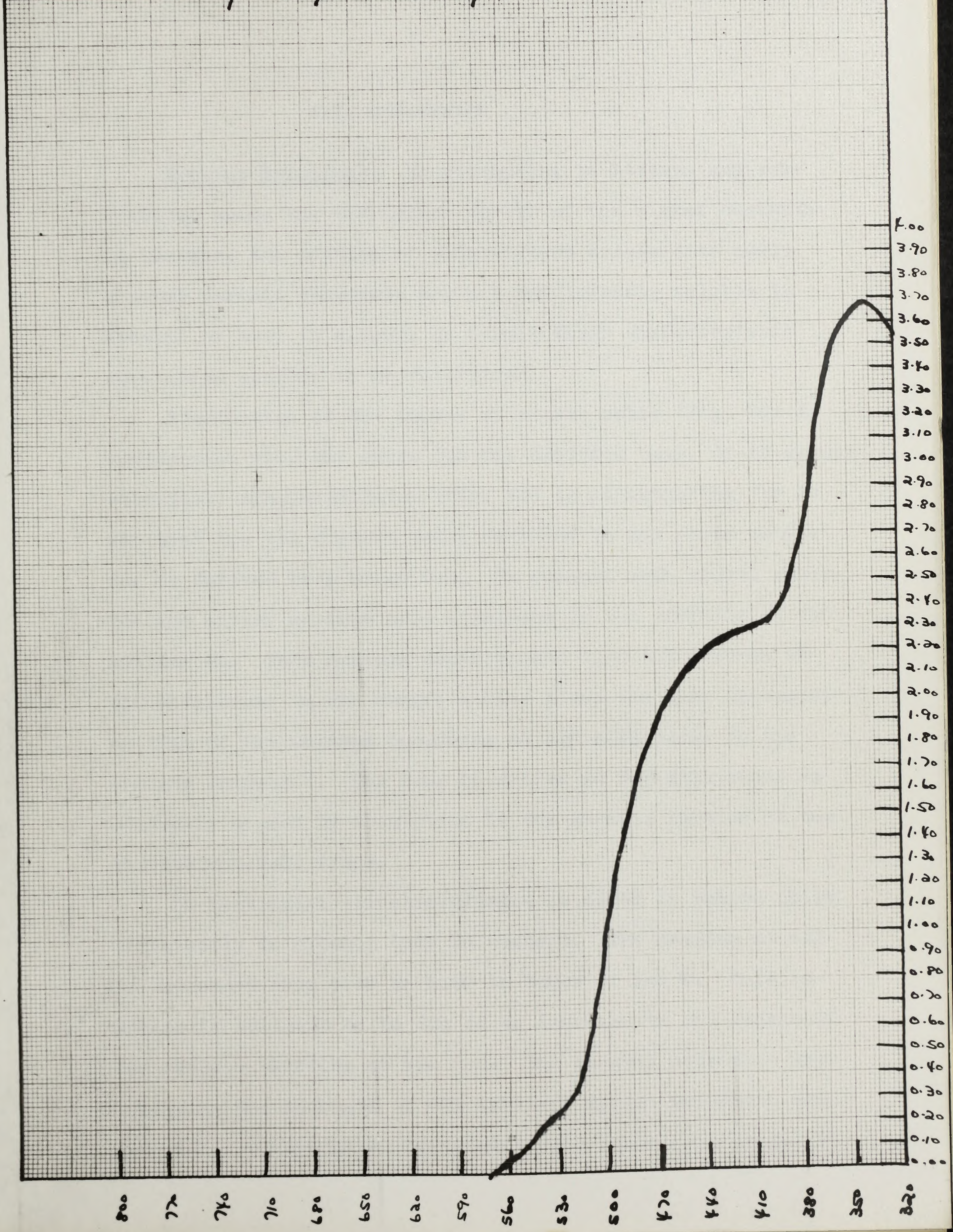
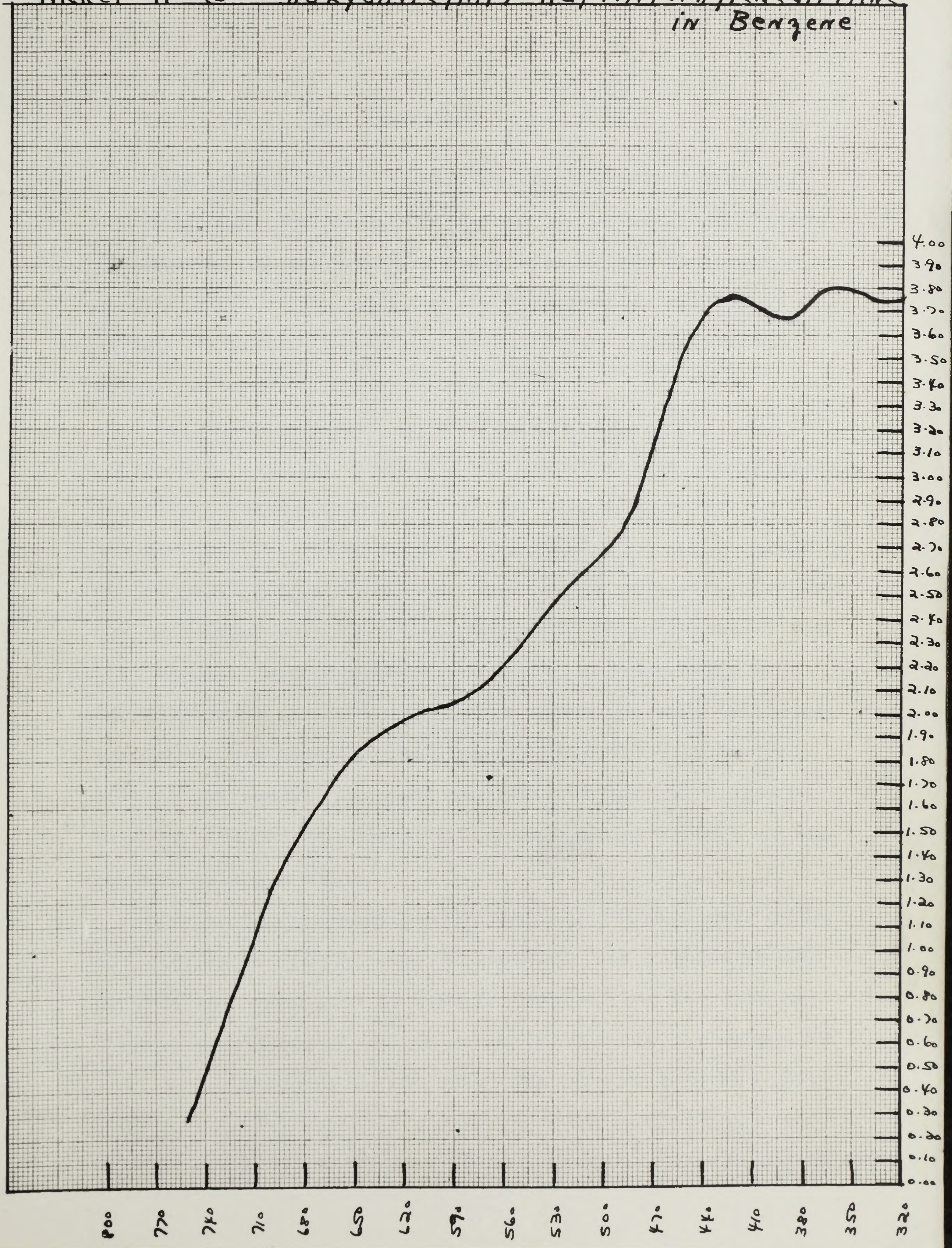


Fig. 46

Nickel di-(3-ethoxysalicylal)-Heptamethylenediimine in Benzene



III. DISCUSSION

Benzene Solutions. In attempting to discern any correlation among the extinction curves of the nickel chelates in benzene, the problem of solubilities arises once again because certain compounds are not sufficiently soluble in benzene or even in alcohol to permit their characteristic absorption spectra to be determined.

Examination of the curves of nickel salts (Fig. 20) in conjunction with the curve for the Schiff's base, di-(3-ethoxysalicylal)-ethylenediimine (Fig. 44) is illuminating for we see that the two highest peaks obtained in the other curves can be derived from these two. In ethanol both nickel chloride and nickel acetate have a maximum in the vicinity of 410 millicrons. This maximum superimposed upon the maximum at 410 millicrons in the Schiff's base gives the same intensity as that of the maximum occurring at 425 millicrons in the chelate compounds. The peak occurring at 335 millicrons is evidently caused by absorption in the organic portion of the chelate molecule alone.

Di-(salicylal)-ethylenediimine is noted to behave quite differently in alcohol than in benzene. The maximum at 410 is increased from 1.50 to 2.90 in terms of log E. This increase is believed to be due to an increase in the amount of the chelate exisitng as the ion. The alcohol acts as a base taking up the hydrogen of the hydroxyl groups leaving a chelate ion. Others have stated that this absorption is due to

formation of a hydrogen bridge with the unshared pair of electrons on the nitrogen atom (cf. supra p.8), but an intramolecular effect of this type would be expected to be greater in benzene than in alcohol in which solvent the unshared pair on the oxygen atom would compete with the nitrogen for the hydrogen.

Furthermore, experiments in this laboratory have shown that formation of the sodium salt of a particular chelate by addition of sodium hydroxide caused an increase in the intensity of this maximum as well as a shift to longer wavelengths (19).

For these reasons it is believed that the bond existing between nickel and oxygen in the chelate is of considerable ionic character since the electron distribution is such that the extinction curve is essentially a summation of the curves for nickel and the chelate ion. The discussion to follow will attempt to show how the ionic character of this bond varies from one compound to another.

¶ Although all the nickel chelates discussed here are known to have square planar configurations as evidenced by their diamagnetism in the solid state, other investigators have found some evidence that in solution some of these same compounds are paramagnetic. This indicates that in solution not all of these compounds retain their planar form. (8)

It is convenient to use nickel di-(3-ethoxysalicylal)-

ethylenediimine as the starting point for this phase of the discussion since it is known to be the most stable of the chelates. Duffield and Calvin in their work on rates of exchange of a radioactive copper isotope with inner complexes of copper showed that the chelate formed with ethylene diamine was the most stable.

The maximum occurring at 545 millimicrons in the curve for nickel di-(3-ethoxysalicylal)-ethylenediimine (Fig. 24) can be assumed to be due to nickel held in the square planar configuration.

This view that the ethylene diamine substituted compound is square planar is substantiated by the work of Mellor (8) in which he found that in non-pyridine solvents no magnetic moment was found for this compound.

Consideration of the extinction curve for nickel di-(3-ethoxysalicylaldimine) shows that this compound is similar in its behavior. The particular maximum being discussed is seen to be slightly shifted to 575 millimicrons as well as being diminished in intensity. A perceptible minimum is evident at 515 millimicrons. Evidently the imine compound is not as stable in its configuration as the ethylenediimine compound because of the changes noted. This idea will be discussed more fully below.

A curve for nickel di-(3-ethoxysalicylalmethylimine) (Fig. 22) and that for nickel di-(3-ethoxysalicylal)-nonamethylenediimine (Fig. 29) are remarkable in their similar-

ity when we consider the differences in their structure. Both have a minimum at 545 millicrons, the region where the other compounds had a maximum, and the maximum is shifted to 620 millimicrons. It is proposed that this shift is characteristic of nickel in a tetrahedral configuration where the nickel-oxygen bond is entirely ionic. This reasoning would presume that the maximum of the paramagnetic simple nickel salts has been shifted to a shorter wave length.

Evidence for this theory that these compounds are not planar but tetrahedral in their configuration is borne out by the magnetic measurements of Mellor (8), who found that the methylimine compound in non-pyridine solvents had a magnetic moment intermediate between that of a square planar configuration and a tetrahedral one.

Steric repulsion between the two methyl groups of the nickel di-(3-ethoxysalicylalmethylimine) probably accounts for the similarity between it and the compound derived from nonamethylenediamine which has a long chain of methylene groups to be accomodated in the space between the two nitrogen atoms. Each of these may possibly be twisted to some extent from its square planar configuration in the solid state to one approaching the tetrahedral configuration in the solution.

Nickel di-(3-ethoxysalicylal)-heptamethylenediimine falls in the same class as the methylimine and nonamethylenediimine compounds since the nickel band is shifted to 620 millimicrons. Here there is no minimum in evidence

which is surprising in view of the shift in the nickel band. Possibly the minimum we would expect to find is obscured by absorption in a region not previously noted, Like the other members of its group, though, the compound is apparently unstable in its configuration to a certain extent in solution. Possibly seven methylene groups is the maximum number that can be accomodated in the chelate molecule before the strain becomes so great as to cause a decided departure from the square planar configuration.

The shifts noted in the curve of nickel di-(3-ethoxysalicylaldiimine) are thought to be due to another effect which causes the compound to have characteristics of both groups. Presumably the compound is less stable than the ethylenediimine compound and this is probably because the two halves of the chelate molecule are not tied together by a methylene bridge.

The portionsof the curves of nickel di-(3-ethoxysalicylal)-trimethylenediimine and nickel di-(3-ethoxysalicylal pentamethylenediimine that could be obtained in benzene are insufficient to permit deductions as to their structure.

A Comparison of the extinction curves of the chelates derived from nickel disalicylaldehyde and those derived from nickel di-(3-ethoxysalicylaldehyde) revealed that they were identical. The substitution of the ethoxy group in the three position has no perceptible effect on the absorption of these chelates.

Pyridine Solutions. As a solvent pyridine is preferable to benzene since all the compounds in the series dissolve sufficiently to give concentrations suitable for absorption spectra work.

The curve for the Schiff's base, di-(3-ethoxysalicylal)-ethylenediimine, has a maximum at 410 millimicrons with an intensity of 2.30, an increase of 0.40 from that observed in benzene (Fig. 45). As in the case of the alcohol solution this increase is believed to be due to absorption by the chelate ion. The pyridine acts as a base to accept the protons from the hydroxyl groups on the benzene rings of the molecule. It was found that Beer's Law was not obeyed in the region 375-400 mmu. This is no doubt caused by the variation in amount of chelates ion present with the concentration of Schiff's base.

Both the hexahydrate and dihydrate of nickel chloride absorb in the same fashion (Figs. 29 & 30). The latter is more difficultly soluble so that the maximum at 650 mmu. cannot be plotted as accurately as for the hexahydrate but the points plotted indicate that some absorption is taking place.

Examination of the curve for the parent compound of the series, nickel di-(3-ethoxysalicylaldehyde), reveals that the nickel maximum at 650 millimicrons has not shifted appreciably (Fig. 31). The maximum in the nickel spectrum at 395 mmu. appears to have added to the maximum in the Schiff's base in

this same region to produce the peak at 410 mmu. This is the same phenomenon observed for solutions of the nickel chelates in benzene. The nickel maximum at 320 mmu. is apparently shifted to shorter wave-lengths since the maximum at 340 mmu. is not increased on going from the Schiff's base to the chelate.

The minimum between 510 and 520 mmu. in Fig. 31 and the lack of any shift in the nickel band is interpreted to mean that the nickel di-(3-ethoxysalylaldehyde) is entirely dissociated in pyridine. This is not surprising in view of the fact that the compound is known to be paramagnetic in the solid state and is therefore tetrahedral in its configuration with ionic type bonds.

Nickel di-(3-ethoxysalicylaldehyde)-ethylenediimine is believed to be the most stable of the series of nickel chelates in pyridine solution as well as in benzene. The extinction curves obtained in the two different solvents are identical with the nickel band appearing at 560 mmu. in pyridine as it did in benzene.

As before we find the series of nickel chelates can be divided into two groups, those whose extinction curves resemble the curve for nickel di-(3-ethoxysalicylaldehyde) and the ones whose curves are similar to the extinction curve of the ethylenediimine compound.

In this first group we find the compounds derived from methyl amine (Fig. 32), hexamethylene diamine (Fig.37),

nonamethylene diamine (Fig. 39), and decamethylene diamine (Fig. 40). These extinction curves are similar in that they have a maximum at about 610 millicrons and a minimum at 510 millicrons. This is evidently the same maximum as that found in the curve of simple nickle salts slightly shifted to a shorter wave length.

Since the nickel-pyridine complex ion absorbs in the same region as these compounds, it is reasonable to conclude that in pyridine solution these compounds are nearly 100% dissociated to give nickel-pyridine ions and chelate ions. That the dissociation is nearly complete is substantiated by the findings of Mellor (8), who reports that in pyridine nickel di-(salicylalmethylimine) has a magnetic moment corresponding to a structure with two unpaired electrons. His theory to account for this is that two pyridine molecules in conjunction with the chelate molecule form a new octahedral complex in which the bonds are of the extreme ionic type.

Mellor also states in this same paper that the results of a few conductivity measurements of pyridine solutions of the nickel chelates indicate that the extent of dissociation is insufficient to account for the observed magnetic moment. This phase of his experiments is not fully described so it is difficult to know how much consideration to give this data.

Because of the distinct resemblance of these curves to that for a simple nickel salt, it seems equally reasonable to postulate a nearly complete dissociation of the nickel

chelate into nickel ions and chelate ions which would account for both the nature of the absorption and the observed magnetic moment.

Turning our attention now to the second group, whose curves resemble that of nickel di-(3-ethoxysalicylal)-ethylene diimine we find that the compounds derived from ammonia, trimethylenediimine, pentamethylene diamine, and heptamethylene diamine are similar. In all of these the nickel band has a maximum at 570 mmu. In the series of chelates whose two halves are tied together by a chain of methylene groups we also note a progressive increase in the intensity of the maximum in going up the series. All of these compounds also absorb in the region above 680 mmu. although the exact nature of the absorption is difficult to determine exactly bacause of the impossibility of obtaining these solutions in high enough concentrations.

In this group of compounds the extent of dissociation is apparently of an entirely different order of magnitude than in the first group of chelates discussed. The idea that there is some dissociation taking place in the pyridine solutions is supported by the fact that the compounds absorb beyond 680 mmu. in the same manner as the nickel chloride. If the change in the nature of the absorption were entirely due to a shift from a square planar to a tetrahedral configuration as proposed for the benzene solutions, we would not expect to find any absorption beyond 680 millimicrons since in benzene all absorption ceases at this point.

It is unfortunate that samples of the tetramethylene and octamethylene diamine substituted compounds were not available since we have data for only three chelates having an even number of methylene groups linking the two halves of the molecule. In the second group consisting of the more stable chelates, it is interesting to note that the compounds having an odd number of methylene groups in the chain appear to the exclusion of the compounds having an even number. This suggests that the odd numbered chain conforms more easily to the spatial requirements of the molecule than does the even numbered chain. This apparently is true only until the chain becomes so long that it forces the two halves of the molecule out of the co-planar position for we find that the nonamethylene compound falls in the class of the compounds that appear to be nearly 100% dissociated.

Nickel di-(3-ethoxysalicylaldimine)falls in the more stable class as we might expect since there is sufficient room to accomodate the hydrogens attached to the nitrogen atoms. The methyl imine compound falls in the opposite class since the methyl groups bulk large enough to cause steric repulsion and the two halves of the molecule become twisted from their previous coplanar position.

As in the work with benzene solutions the extinction curves of the chelates prepared from nickel di-(3-ethoxysalicylaldehyde) are identical with the curves of the chelates prepared from nickel disalicylaldehyde. The ethoxy group does not affect the absorption in any way.

CHAPTER V

SUMMARY

On the basis of an initial broad survey of the type undertaken here, one is hardly justified in drawing definite conclusions as to the structure of specific compounds. It is possible, however, to make certain broad statements concerning the possible reasons for their behavior.

The polarographic technique was shown to be of value in determining the stability of a few of the members of the nickel chelate series but the solubility characteristics of these compounds are such that only limited information can be obtained in this way. We did find that, in agreement with the work previously done on the copper chelates, tying together the two halves of the molecule increases the stability. Also the comparison between the nickel di-(salicylal)-ethylenediimine and nickel di-(salicylal)-pentamethylenediimine shows the latter to be less stable of the two. Also some evidence was found that nickel di-(salicylalmethylimine) and nickel di-(salicylal-dimine) are dissociated in pyridine.

The investigation of the light absorption of the nickel chelates was more fruitful for it was possible to study a greater number of compounds. The investigation of the chelates in benzene indicates that steric factors within the chelate molecule in solution are important in predicting whether or not the molecule will retain the square planar

configuration it has in the solid state.

In the investigation of the properties in pyridine solution evidence was found that the same compounds believed to shift to a tetrahedral configuration in benzene solution are nearly wholly dissociated in pyridine. Other members of the series appeared to be dissociated to a much smaller degree and there seemed to be a correlation between this fact and the number of methylene groups in the chain linking the two halves of the molecule. Evidently the methylene chains with an odd number of groups lend themselves better to a stabler coplanar configuration than do the chains having an even number of methylene groups. Beyond seven methylene groups the length of the chain rather than its packing becomes the dominant factor.

<u>Suggestions for Further Investigation.</u> A considerable amount of additional work would be necessary to determine accurately the importance of the various factors involved in the structure of these chelates. Absorption cells having a longer light path would be useful to obtain more accurate data in the regions where absorption is low. With these cells it would also be possible to use more dilute solutions of several different concentrations to determine if the compounds obey Beer's Law. If it were found that the compounds did not obey Beer's Law then we would have further proof that the nickel chelates dissociate. It would also be desirable to study the change in the extinction curves with temperature since this would show if an equilibrium really does exist between two molecular species.

APPENDIX

NICKEL CHLORIDE HEXAHYDRATE IN ALCOHOL

0.01 M

Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.011	1.1	0.04	630	0.003	0.3	-
330	0.008	0.8	-	640	0.004	0.4	-
340	0.007	0.7	-	650	0.007	0.7	-
350	0.008	0.8	-	660	0.007	0.7	-
360	0.008	0.8	-	670	0.009	0.9	-
370	0.007	0.7	-	680	0.010	1.0	-0.00
380	0.013	1.3	0.11	690	0.012	1.2	0.08
390	0.021	2.1	0.32	700	0.012	1.2	0.08
400	0.034	3.4	0.53	710	0.012	1.2	0.08
410	0.047	4.7	0.67	720	0.012	1.2	0.08
420	0.054	5.4	0.73	730	0.014	1.4	0.15
430	0.047	4.7	0.67	740	0.015	1.5	0.18
440	0.036	3.6	0.56	750	0.016	1.6	0.20
450	0.025	2.5	0.40	760	0.017	1.7	0.23
460	0.019	1.9	0.28	770	0.017	1.7	0.23
470	0.010	1.0	0	780	0.018	1.8	0.26
480	0.007	0.7	-	790	0.017	1.7	0.23
490	0.004	0.4	-	800	0.017	1.7	0.23
500	0.003	0.3	-	810	0.015	1.5	0.18
510	0.003	0.3	-	820	0.014	1.4	0.15
520thru	0	0	-	830	0.013	1.3	0.11
620	0	0	-	840	0.010	1.0	0

NICKEL ACETATE TETRAHYDRATE IN ALCOHOL

0.002 M

Wave Length	D	E	Log E
320	0.007	3.5	0.54
330	0.004	2.0	0.30
340	0.004	2.0	0.30
350	0.007	3.5	0.54
360	0.007	3.5	0.54
370	0.008	4.0	0.60
380	0.013	6.5	0.81
390	0.020	10.0	1.00
400	0.023	11.5	1.06
410	0.027	15.5	1.19
420	0.019	9.5	0.98
430	0.013	6.5	0.81
440	0.010	5.0	0.70
450	0.007	3.5	0.54
460	0.006	3.0	0.48
470	0.004	2.0	0.30
500	0.0025	1.25	0.10

This data taken from the unpublished experiments of L.Reuben.

NICKEL DI-(3-ETHOXYSALICYLALDEHYDE) IN ALCOHOL

0.0002 M

Wave Length	D	E	log E	Wave Length	D	D	log E
320	0.176	880	2.95	530	0.005	25	1.40
330	0.204	1020	3.01	540	0.006	30	1.48
340	0.229	1145	3.06	550	0.005	25	1.40
350	0.237	1185	3.07	560	0.004	20	1.30
360	0.230	1150	3.07	570	0.003	15	1.18
370	0.220	1110	3.05	580	0.003	15	1.18
380	0.216	1080	3.03	590	0.003	15	1.18
390	0.224	1120	3.05	600	0.003	15	1.18
400	0.226	1130	3.05	610	0.003	15	1.18
410	0.217	1085	3.04	620	0.006	30	1.48
420	0.183	915	2.96	630	0.005	25	1.40
430	0.141	705	2.85	640	0.002	10	1.00
440	0.094	275	2.44	650 thru	0.002	10	1.00
450	0.050	250	2.40	730	0.002	10	1.00
460	0.028	140	2.15	740	0.001	5	0.70
470	0.017	85	1.93	750	0.001	5	0.70
480	0.012	60	1.78	760	0.001	5	0.70
490	0.010	50	1.70	770	0.001	5	0.70
500	0.008	40	1.60				
510	0.007	35	1.54				
520	0.006	30	1.48				
530	0.005	25	1.40				
540	0.006	30	1.48				

NICKEL DI-(3-ETHOXYSALICYLALDIMINE)

IN BENZENE

0.00005 M				0.0005 M			
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.370	7400	3.87	470	0.200	400	2.60
330	0.455	9100	3.96	480	0.092	184	2.27
340	0.511	10220	4.01	490	0.053	106	2.03
350	0.291	3820	3.58	500	0.040	80	1.90
360	0.120	2400	3.38	510	0.035	70	1.85
370	0.083	1660	3.22	520	0.035	70	1.85
380	0.084	1680	3.23	530	0.036	72	1.86
390	0.100	2000	3.30	540	0.042	84	1.92
400	0.125	2500	3.40	550	0.046	92	1.96
410	0.160	3200	3.51	560	0.048	96	1.96
420	0.177	3540	3.55	570	0.048	96	1.96
430	0.160	3200	3.51	580	0.048	96	1.96
440	0.177	2920	3.47	590	0.037	74	1.87
450	0.109	2180	3.34	600	0.030	60	1.73
460	0.058	1160	3.07	610	0.030	60	1.78
470	0.033	660	2.82	620	0.027	54	1.73
480	0.019	380	2.58	630	0.020	40	1.60

NICKEL DI-(3-ETHOXYSALICYLALDIMINE)

IN BENZENE

0.0005 M (cont.)

Wave Length	D	E	log E
640	0.013	26	1.42
650	0.010	20	1.30
660	0.008	16	1.20
670	0.007	14	1.15
680	0.006	12	1.08
690	0.006	12	1.00
700	0.006	12	1.08
725	0.005	10	1.00
750	0.005	10	1.00
775	0.005	10	1.00
800	0.005	10	1.00
850	0.004	6	0.78
900	0.002	4	0.60

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NICKEL DI-(3-ETHOXYSALICYLALDIMINE) IN BENZENE

0.0001 M				0.001 M			
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.392	7840	3.89	430	1.715	3430	3.54
330	0.492	9840	3.99	440	1.515	3030	3.48
340	0.553	11060	4.04	450	1.114	2228	3.35
350	0.316	7320	3.87	460	0.521	1042	3.02
360	0.124	2480	3.39	470	0.203	406	2.61
370	0.083	1660	3.22	480	0.089	178	2.25
380	0.087	1640	3.21	490	0.054	108	2.03
390	0.100	2000	3.30	500	0.039	78	1.89
400	0.129	2580	3.41	510	0.033	66	1.82
410	0.171	3420	3.53	520	0.033	66	1.82
420	0.187	3740	3.57	530	0.035	70	1.85
430	0.147	3340	3.52	540	0.038	76	1.88
440	0.150	3000	3.48	550	0.043	86	1.94
450	0.112	2240	3.35	560	0.045	90	1.95
460	0.053	1060	3.03	570	0.045	90	1.95
470	0.022	440	2.64	580	0.045	90	1.95

The extinction curve of this compound was obtained a second time to discover if, unlike other benzene solutions of the nickel chelates it absorbed in the region above 700 millimicrons. This second trial shows the first data to be in error above 650 millicrons.

NICKEL DI-(3-ETHOXYSALICYLALDIMINE) IN BENZENE

0.001 M (cont.)

Wave Length	D	E	log E
590	0.041	82	1.91
600	0.037	74	1.87
610	0.030	60	1.78
620	0.021	42	1.62
630	0.017	34	1.53
640	0.011	22	1.34
650	0.008	16	1.20
660	0.007	14	1.15
670	0.004	8	0.90
680	0.003	6	0.78
690	0.003	6	0.78
700	0.002	4	0.60
710	0.001	2	0.30
720	0.001	2	0.30
730	0.001	2	0.30
740	0.001	2	0.30
750	0.001	2	0.30
760	0	0	-
770	0	0	-
780	0	0	-
790	0	0	-
800	0	0	-

NICKEL DI-(3-ETHOXYSALICYLALMETHYLIMINE)

IN BENZENE

0.0001 M				0.001 M			
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.665	6650	3.82	470	0.300	300	2.48
330	0.795	7950	3.90	480	0.178	178	2.25
340	0.780	7800	3.89	490	0.139	139	2.14
350	0.442	4420	3.65	500	0.113	113	2.05
360	0.250	2500	3.40	510	0.095	95	1.98
370	0.068	680	2.83	520	0.078	78	1.89
380	0.208	2080	3.32	530	0.063	63	1.80
390	0.246	2460	3.39	540	0.057	57	1.76
400	0.282	2820	3.45	550	0.052	52	1.71
410	0.332	3220	3.51	560	0.052	52	1.72
420	0.365	3650	3.56	570	0.068	68	1.83
430	0.341	3410	3.53	580	0.065	65	1.81
440	0.275	2750	3.46	590	0.074	74	1.87
450	0.162	1620	3.21	600	0.081	81	1.91
460	0.070	700	2.85	610	0.087	87	1.94
470	0.030	300	2.48	620	0.088	88	1.95
480	0.020	200	2.30	630	0.086	86	1.94
490	0.015	150	2.18	640	0.080	80	1.90

NICKEL DI-(3-ETHOXYSALICYLALMETHYLIMINE)

IN BENZENE

0.001 M (cont)

Wave Length	D	E	Log E.
650	0.071	71	1.85
660	0.058	58	1.76
670	0.047	47	1.67
680	0.035	35	1.54
690	0.025	25	1.40
710	0.016	16	1.08
720	0.008	8	0.90
730	0.005	5	0.70
740	0.004	4	0.60
750	0.002	2	0.30
760	0.002	2	-
770	0	0	-
780	0	0	-
790	0.	0	-
800	0	0	-

NICKEL DI-(3-ETHOXYSALICYLAL)-ETHYLENEDIIMINE

IN BENZENE

0.0001M				0.00025 M			
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.820	8200	3.91	475	0.530	2120	3.33
330	0.880	8800	3.94	480	0.340	1360	3.13
340	0.855	8550	3.93	490	0.157	630	2.80
350	0.820	8200	3.91	500	0.083	332	2.52
360	0.640	6400	3.81	510	0.040	160	2.20
370	0.325	3250	3.51	520	0.052	208	2.32
380	0.274	2740	3.44	530	0.052	208	2.32
390	0.345	3450	3.54	540	0.052	208	2.32
400	0.425	4250	3.63	550	0.047	188	2.27
405	0.468	4680	3.67	560	0.043	172	2.24
410	0.540	5400	3.73	570	0.042	172	2.24
415	0.645	6450	3.81	580	0.034	136	2.13
420	0.720	7200	3.86	590	0.027	108	2.03
425	0.710	7100	3.85	600	0.020	80	1.90
430	0.640	6400	3.81	610	0.015	60	1.78
440	0.462	4620	3.67	620	0.012	48	1.68
450	0.382	3820	3.58	630	0.004	16	1.20
460	0.335	3350	3.53	640	0.002	8	0.90
470	0.260	2600	3.42	650	0.002	8	0.90
475	0.203	2030	3.31	675	0.002	8	0.90
480	0.118	1180	3.07	700	0	0	-
490	0.065	650	2.81	725	0	0	-

NICKEL DI-(3-ETHOXYSALICYLAL)-TRIMETHYLENEDIIMINE DIHYDRATE

IN BENZENE

0.0001 M

Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.452	4520	3.66	520	0.026	260	2.42
330	0.444	4440	3.65	530	0.023	230	2.36
340	0.463	4630	3.67	540	0.017	170	2.20
350	0.532	5320	3.73	550	0.013	130	2.11
360	0.590	5900	3.77	560	0.012	120	2.08
370	0.580	5800	3.76	570	0.008		
380	0.455	4550	3.66	580	0.007		
390	0.343	3430	3.54	590	0.007		
400	0.351	3510	3.55	600	0.007		
410	0.380	3800	3.58	610	0.007		
420	0.423	4230	3.63	620	0.005		
430	0.458	4580	3.66	630	0.007		
440	0.415	4150	3.62	640	0.005		
450	0.307	3070	3.49	650	0.005		
460	0.205	2050	3.31	660	0.002		
470	0.123	1230	3.21	670	0.003		
480	0.076	760	2.88	680	0.001		
490	0.051	510	2.71	690	0.002		
500	0.040	400	2.60	700	0.002		
510	0.033	330	2.52	71			

Data obtained at wave lengths above 570 millimicrons not plotted because the solution does not absorb sufficiently to give accurate readings.

NICKEL DI-(3-ETHOXYSALICYLAL)-TRIMETHYLENEDIIMINE

IN BENZENE

0.0001 M

Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.509	5090	3.71	470	0.135	5090	3.13
330	0.488	4880	3.69	480	0.082	4880	2.91
340	0.519	5190	3.72	490	0.056	5190	2.75
350	0.590	5900	3.77	500	0.044	440	2.64
360	0.655	6550	3.82	510	0.035	350	2.54
370	0.640	6400	3.81	520	0.031	310	2.49
380	0.499	4990	3.70	530	0.023	230	2.36
390	0.377	3770	3.58	540	0.020	200	2.30
400	0.389	3890	3.59	550	0.016	160	2.20
410	0.425	4250	3.63	560	0.013	130	2.11
420	0.468	4680	3.67	570	0.010	100	2.00
430	0.505	5050	3.70	580	0.008	80	1.90
440	0.453	4530	3.66	590	0.008	80	1.90
450	0.332	3320	3.52				
460	0.223	2230	3.35				

NICKEL DI-(3-ETHOXYSALICYLAL)-PENTAMETHYLENEDIIMINE

IN BENZENE

0.00005 M

Wave Length	D	E	log E
320	0.257	5140	3.71
330	0.264	5280	3.72
340	0.300	6000	3.78
350	0.348	6960	3.84
360	0.375	7500	3.88
370	0.292	5840	3.77
380	0.166	3320	3.52
390	0.145	2900	3.46
400	0.171	3420	3.53
410	0.200	4000	3.60
420	0.245	4900	3.69
430	0.256	5120	3.71
440	0.209	4180	3.62
450	0.169	3380	3.53
460	0.132	2640	3.42
470	0.080	1600	3.20
480	0.038	760	2.88
490	0.021	420	2.62
500	0.013	260	2.42
510	0.010	200	2.30
520	0.009	180	2.26

NICKEL DI-(3-ETHOXYSALICYLAL)-HEPTAMETHYLENEDIIMINE

IN BENZENE

0.0001 M				0.001 M			
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.579	5790	3.76	460	2.21	2210	3.34
330	0.568	5680	3.75	470	1.323	1323	3.12
340	0.573	5730	3.76	480	0.816	816	2.91
350	0.597	5970	3.78	490	0.579	579	2.76
360	0.618	6180	3.79	500	0.468	468	2.67
370	0.602	6020	3.78	510	0.411	411	2.61
380	0.524	5240	3.72	520	0.356	356	2.55
390	0.452	4520	3.66	530	0.302	302	2.48
400	0.463	4630	3.67	540	0.247	247	2.39
410	0.498	4980	3.70	550	0.202	202	2.31
420	0.544	5440	3.74	560	0.163	163	2.21
430	0.565	5650	3.75	570	0.137	137	2.14
440	0.496	4960	3.70	580	0.122	122	2.09
450	0.358	3580	3.55	590	0.112	112	2.05
460	0.228	2280	3.36	600	0.104	104	2.02
470	0.133	1330	3.12	620	0.094	94	1.97
480				630	0.086	86	1.93
				640	0.076	76	1.88
				660	0.055	55	1.74
				680	0.033	33	1.52
				700	0.018	18	1.26
				725	0.006	6	0.78
				750	0.002	2	0.30

NICKEL DI-(3-ETHOXYSALICYLAL)-NONAMETHYLENEDIIMINE

IN BENZENE

0.0001 M				0.0005 M			
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.395	3950	3.60	430	1.03	2060	3.31
330	0.458	4580	3.66	440	0.656	1312	3.12
340	0.449	4490	3.65	450	0.670	1340	3.13
350	0.310	3100	3.49	460	0.320	640	2.81
360	0.193	1930	3.29	470	0.145	290	2.46
370	0.145	1450	3.16	480	0.080	160	2.20
380	0.143	1430	3.16	490	0.056	112	2.05
390	0.160	1600	3.20	500	0.048	96	1.98
400	0.175	1750	3.24	510	0.042	84	1.92
410	0.199	1990	3.30	520	0.037	74	1.87
420	0.209	2090	3.32	530	0.033	66	1.82
430	0.186	1860	3.27	540	0.031	62	1.79
440	0.152	1520	3.18	550	0.031	62	1.75
450	0.099	990	3.00	560	0.031	62	1.79
460	0.044	440	2.64	570	0.028	56	1.75
470	0.037	370	2.57	580	0.034	68	1.83
				590	0.035	70	1.85
				600	0.038	74	1.87
				610	0.039	78	1.89
				620	0.041	82	1.91
				630	0.041	82	1.91
				640	0.039	78	1.89
				650	0.035	70	1.85

NICKEL DI-(3-ETHOXYSALICYLAL)-NONAMETHYLENEDIIMINE IN BENZENE

0.0005 M (cont.)

Wave Length	D	E	log E
660	0.030	60	1.78
670	0.025	50	1.70
680	0.019	38	1.58
690	0.014	28	1.45
700	0.011	22	1.34
710	0.007	14	1.15
720	0.005	10	1.00
730	0.003	6	0.78
740	0.001	2	0.30
750	0	0	-
760	0	0	-
770	0	0	-
780	0	0	-
790	0	0	-
800	0	0	-

DI-(SALICYLAL)-ETHYLENEDIIMINE IN ALCOHOL

0.0001 M				0.001 M			
Wave Length	D	E	log E	Wave length	D	E	log E
320	0.790	7900	3.90	360	0.522	522	2.72
330	0.600	6000	3.78	370	0.461	461	2.66
340	0.298	2980	3.47	380	0.540	540	2.73
350	0.117	1170	3.07	390	0.651	651	2.81
360	0.063	630	2.80	400	0.740	740	2.87
370	0.055	550	2.74	410	0.750	750	2.88
380	0.063	630	2.80	420	0.670	670	2.83
390	0.070	700	2.85	430	0.510	510	2.71
				440	0.322	322	2.51
				450	0.158	158	2.20
				460	0.055	55	1.74
				470	0.012	12	1.08
				480	0.002	2	0.30
				490	0.001	1	0
				800	0.001	1	0

DI-(SALICYLAL)-ETHYLENEDIIMINE IN BENZENE

Wave Length	D	E	log E	Wave Length	D	E	log E
	0.0001 M					0.01 M	
320	0.950	9500	3.98	380	0.651	65.1	1.81
330	0.818	8180	3.91	390	0.410	41	1.61
340	0.435	4350	3.64	400	0.325	32.5	1.51
350	0.152	1520	3.18	410	0.283	28.3	1.45
360	0.057	570	2.76	420	0.250	25.0	1.40
				430	0.203	20.3	1.31
	0.001 M						
360	0.410	410	2.61	440	0.158	15.8	1.20
370	0.147	147	2.17	450	0.111	11.1	1.05
380	0.075	75	1.88	460	0.063	6.3	0.80
390	0.048	48	1.68	470	0.025	2.5	0.40
400	0.036	36	1.56	480	0.008	0.8	-
410	0.020	20	1.30	490	0.001	0.1	-
				thru			
				800	0.001	0.1	-

DI-(3-ETHOXYSALICYLAL)-ETHYLENEDIIMINE IN BENZENE

Wave Length	D	E	log E	Wave Length	D	E	log E
	0.0001 M					0.01 M	
320	0.340	3400	3.53	390	1.565	56.5	2.19
330	0.420	4200	3.62	400	0.899	89.9	1.95
340	0.408	4080	3.61	410	0.700	70.0	1.85
350	0.323	3230	3.51	420	0.645	64.5	1.81
360	0.190	1900	3.28	430	0.604	60.4	1.78
370	0.080	800	2.90	440	0.549	54.9	1.74
380	0.027	270	2.43	450	0.475	47.5	1.68
390	0.009	90	1.95	460	0.372	37.2	1.57
				470	0.270	24.0	1.38
	0.001 M			480	0.180	18.0	1.26
370	1.027	1027	3.01	490	0.099	9.9	1.00
380	0.392	392	2.59	500	0.044	4.4	0.64
390	0.172	172	2.24	510	0.016	1.6	0.20
400	0.105	105	2.02	520	0.007	0.7	-
410	0.077	77	1.89	530	0.004	0.4	-
420	0.070	70	1.85	540	0.002	0.2	-
430	0.065	65	1.81	550	0.002	0.2	-
440	0.057	57	1.76	560	0.001	0.1	-
450	0.048	48	1.68	570	0.001	0.1	-
460	0.039	39	1.59	580	0.001	0.1	-
470	0.027	27	1.43	590	0	0	-
480	0.019	19	1.28	600	0	0	-
490	0.010	10	1.00				

NICKEL CHLORIDE HEXAHYDRATE IN PYRIDINE

Wave Length	D	E	log E
	0.001 M		
320	0.126	126	2.10
330	0.094	94	1.97
340	0.056	56	1.75
350	0.028	28	1.48
	0.01 M		
340.	0.530	53	1.72
350	0.230	23	1.36
360	0.102	102	1.01
370	0.070	70	0.85
380	0.075	75	0.88
390	0.088	88	0.95
400	0.082	82	0.91
410	0.064	64	0.81
420	0.048	48	0.68
430	0.032	32	0.51
440	0.022	22	0.34
450	0.017	17	0.23
460	0.017	17	0.23
470	0.013	13	0.11
480	0.013	13	0.11
490	0.011	11	0.04
500	0.012	13	0.08
	0.01 M (cont.)		
510	0.010	1.0	0
520	0.013	1.3	0.11
530	0.012	1.2	0.08
540	0.013	1.3	0.11
550	0.014	1.4	0.15
570	0.018	1.8	0.26
580	0.022	2.2	0.34
590	0.026	2.6	0.42
600	0.029	2.9	0.46
610	0.032	3.2	0.51
620	0.038	3.8	0.58
630	0.041	4.1	0.61
640	0.041	4.1	0.61
650	0.041	4.1	0.61
660	0.041	4.1	0.61
670	0.038	3.8	0.58
680	0.036	3.6	0.56
690	0.033	3.3	0.52
700	0.033	3.3	0.52
710	0.030	3.0	0.48
720	0.026	2.6	0.42
730	0.025	2.5	0.40

NICKEL CHLORIDE HEXAHYDRATE IN PYRIDINE

0.01 M (cont.)

Wave length	D	E	log E
740	0.023	2.3	0.36
750	0.021	2.1	0.32
760	0.020	2.0	0.30
770	0.018	1.8	0.26
780	0.017	1.7	0.23
790	0.016	1.7	0.23
800	0.017	1.7	0.23
810	0.017	1.7	0.23
620	0.017	1.7	0.23
630	0.015	1.5	0.18
640	0.017	1.7	0.23
650	0.017	1.7	0.23
860	0.015	1.5	0.18
870	0.016	1.6	0.20
880	0.017	1.7	0.23

NICKEL CHLORIDE DIHYDRATE IN PYRIDINE

Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.256	256	2.41	560	0	0	-
330	0.177	177	2.25	580	0	0	-
340	0.099	99	2.00	600	0.001	1	0
350	0.040	40	1.60	610	0.003	3	0.48
360	0.017	17	1.23	620	0.003	3	0.48
370	0.011	11	1.04	630	0.003	3	0.48
380	0.011	11	1.04	640	0.003	3	0.48
390	0.010	10	1.00	650	0.005	5	0.70
400	0.012	12	1.08	660	0.002	2	0.30
410	0.007	7	0.85	670	0.002	2	0.30
420	0.004	4	0.60	680	0.002	2	0.30
430	0.001	1	0	690	0.002	2	0.30
440	0.001	1	0	700	0.002	2	0.30
450	0.001	1	0	725	0.001	1	0
460	0.001	1	0	750	0	0	-
470	0	0	-	775	0	0	-
480	0	0	-	800	0	0	-
490	0	0	-				
500	0	0	-				
510	0	0	-				
520	0	0	-				
540	0	0	-				

NICKEL DI-(3-ETHOXYSALICYLALDEHYDE)

IN PYRIDINE

	0.0001 M				0.001 M		
Wave Length	D	E	log E	Wave length	D	E	log E
320	.238	2380	3.377	460	.985	985	2.973
330	.308	3080	3.489	470	.267	267	2.427
340	.355	3550	3.550	480	.067	67	1.826
350	.356	3560	3.551	490	.020	20	1.301
360	.339	3390	3.530	500	.006	6	0.778
370	.316	3160	3.500	510	.001	1	0.0
380	.319	3190	3.304	520			
383	.345	3450	3.538	530	-.006		
390	.355	3550	3.550	540	-.005		
400	.385	3850	3.386	550	-.004		
410	.396	3960	3.398	560	-.003		
420	.365	3650	3.562	570	0		
430	.299	2990	3.476	580	.002	2	0.301
440	.218	2180	3.339	590	.004	4	0.602
430	.123	1230	3.090	600	.006	6	0.778
460	.050	500	2.699	610	.007	7	0.903
470	.018	180	2.255	620	.007	7	.903
480	.009	90	1.954	630	.007	7	.903

NICKEL DI-(3-ETHOXYSALICYLALDEHYDE) IN PYRIDINE

.001 M

Wave Length	D	E	log E
640	.007	7	.903
650	.007	7	.845
660	.007	7	.845
670	.0055	5.5	.740
680	.0055	5.5	.740
690	.003	3.	.477
700	.003	3	.477
710	.202	2	.301
720	.001	1	0.0
730	0		
740	0		
750	0		
775	0		
800	0		

NICKEL DI-(3-ETHOXYSALICYLALDIMINE)

IN PYRIDINE

	0.0001 M			0.001 M			
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.408	4080	3.61	460	0.412	412	2.62
330	0.472	4720	3.67	470	0.198	198	2.30
340	0.535	5350	3.73	480	0.102	102	2.01
350	0.464	4640	3.67	490	0.062	62	1.79
360	0.448	4480	3.65	500	0.043	43	1.66
370	0.523	5230	3.72	510	0.024	24	1.38
380	0.600	6000	3.78	520	0.033	33	1.52
390	0.615	6150	3.79	530	0.033	33	1.52
400	0.560	5600	3.75	540	0.037	37	1.57
410	0.438	4380	3.64	550	0.040	40	1.60
420	0.286	2860	3.46	560	0.043	43	1.56
430	0.182	1820	3.26	570	0.043	43	1.48
440	0.133	1330	3.12	580	0.040	40	1.40
450	0.092	920	2.96	590	0.036	36	1.56
460	0.053	530	2.72	600	0.030	30	1.48
470	0.027	270	2.43	610	0.025	25	1.40
480	0.015	150	2.18	620	0.020	20	1.30

NICKEL DI-(3-ETHOXYSALICYLALDIMINE)

IN PYRIDINE

0.001 M

Wave Length	D	E	log E
630	0.015	15	1.18
640	0.012	12	1.08
650	0.008	8	0.90
660	0.004	4	0.60
670	0.003	3	0.48
680	0.004	4	0.60
690	0.002	2	0.30
700	0.002	2	0.30
725	0.002	2	0.30
750	0.004	4	0.60
775	0.005	5	0.69
800	0.006	6	0.78

NICKEL DI-(3-ETHOXYSALICYLALMETHYLIMINE)

IN PYRIDINE

0.0001 M				0.001 M			
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.199	1990	3.30	430	0.550	550	2.74
330	0.223	2230	3.35	440	0.149	149	2.17
340	0.338	3380	3.53	450	0.060	60	1.78
350	0.310	3100	3.49	460	0.038	38	1.58
360	0.376	3760	3.58	470	0.027	27	1.43
370	0.465	4650	3.67	480	0.025	25	1.40
380	0.510	5100	3.71	490	0.014	14	1.15
390	0.508	5080	3.71	500	0.009	9	0.95
400	0.413	4130	3.62	550	0.009	9	0.95
410	0.279	2790	3.45	600	0.010	10	1.00
420	0.133	1330	3.12	625	0.010	10	1.00
430	0.048	480	2.68	650	0.014	14	1.15
440	0.025	250	2.40	675	0.003	3	0.48
				700	0	0	-

NICKEL DI-(3-ETHOXYSALICYLAL)-ETHYLENEDIIMINE IN PYRIDINE

0.0001 M				0.001 M			
Wave Length	D	E	log E	Wave Length	E	E	log E
320	0.568	5680	3.75	480	0.900	900	2.95
330	0.650	6500	3.81	490	0.441	441	2.64
340	0.750	7500	3.88	500	0.255	255	2.41
350	0.820	8200	3.91	510	0.185	185	2.27
355	0.820	8200	3.91	520	0.157	157	2.20
360	0.792	7920	3.90	530	0.138	138	2.14
370	0.534	5340	3.73	540	0.135	135	2.13
380	0.0347	3470	3.54	550	0.131	131	2.12
390	0.333	2220	3.52	560	0.123	123	2.01
400	0.375	3750	3.57	570	0.132	132	2.12
405	0.410	4100	3.61	580	0.116	116	2.07
410	0.835	8350	3.92	590	0.100	100	2.00
415	0.509	5090	3.71	600	0.075	75	1.88
420	0.541	5410	3.73	610	0.055	55	1.74
430	0.473	4730	3.68	620	0.034	34	1.53
440	0.360	3600	3.56	630	0.022	22	1.34
450	0.297	2970	3.47	640	0	0	0
460	0.240	2400	3.38	650	0.007	7	0.85
470	0.157	1570	3.20	660	0.006	6	0.78
480	0.127	1270	3.10	670	0.002	2	0.30
490	0.048	480	2.68	680	0.001	1	0
500	0.058	580	2.76	690	0.001	1	0

NICKEL DI-(3-ETHOXYSALICYLAL)-TRIMETHYLENEDIIMINE

IN PYRIDINE

	0.0001 M				0.001 M		
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.203	2030	3.31	460	0.214	214	2.66
330	0.178	1780	3.25	470	0.094	94	1.97
340	0.203	2030	3.31	480	0.065	65	1.81
350	0.285	2850	3.46	490	0.048	48	1.68
360	0.422	4220	3.63	500	0.040	40	1.51
370	0.600	6000	3.78	510	0.032	32	1.43
380	0.735	7350	3.87	520	0.027	27	1.43
390	0.790	7900	3.90	530	0.024	24	1.38
400	0.750	7500	3.88	540	0.022	22	1.34
410	0.635	6350	3.80	550	0.022	22	1.34
420	0.462	4620	3.67	560	0.022	22	1.34
430	0.284	2840	3.45	570	0.021	21	1.34
440	0.135	1350	3.13	580	0.021	21	1.34
450	0.052	520	2.72	590	0.017	17	1.23
460	0.017	170	2.23	600	0.016	16	1.20
470	0.005	50	1.70	610	0.013	13	1.11

NICKEL DI-(3-ETHOXYSALICYLAL)-TRIMETHYLENEDIIMINE

IN PYRIDINE

0.001 M (cont).

Wave Length	D	E	Log E
620	0.011	11	1.04
630	0.009	9	0.95
640	0.008	8	0.90
650	0.007	7	0.85
660	0.007	7	0.85
670	0.006	6	0.78
680	0.005	5	0.70
690	0.005	5	0.70
700	0.005	5	0.70
710	0.005	5	0.70
720	0.006	6	0.78
730	0.005	5	0.70
740	0.011	11	0.04
750	0.007	7	0.85
775	0.012	12	1.08
800	0.015	15	1.18

NICKEL DI-(3-ETHOXYSALICYLAL)-PENTAMETHYLENENDIIMINE

IN PYRIDINE

0.0001 M				0.001 M			
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.320	3200	3.51	470	0.747	747	2.87
330	0.324	3240	3.51	480	0.395	395	2.60
340	0.376	3760	3.58	490	0.242	242	2.39
350	0.452	4520	3.66	500	0.183	183	2.26
360	0.516	5160	3.71	510	0.144	144	2.16
370	0.490	4900	3.69	520	0.116	116	2.07
380	0.465	4650	3.67	530	0.094	94	1.97
390	0.469	4690	3.67	540	0.079	79	1.90
400	0.452	4520	3.66	550	0.072	72	1.86
410	0.425	4250	3.63	560	0.066	66	1.82
420	0.380	3800	3.58	570	0.064	64	1.81
430	0.292	2920	3.47	580	0.061	61	1.79
440	0.208	2080	3.32	590	0.057	57	1.76
450	0.152	1520	3.18	600	0.050	50	1.70
460	0.105	1050	3.02	610	0.043	43	1.63
470	0.062	620	2.79	620	0.035	35	1.54
480	0.032	320	2.51	630	0.027	27	1.43
490	0.021	210	2.32	640	0.021	21	1.32
500	0.016	160	2.20	650	0.016	16	1.20
510	0.012	120	2.08	660	0.013	13	1.11
520	0.011	110	2.04	670	0.011	11	1.04

NICKEL DI-(3-ETHOXYSALICYLAL)-PENTAMYTHELENEDIIMINE IN PYRIDINE

0.001 M (cont.)

Wave Length	D	E	log E
680	0.009	9	0.95
690	0.009	9	0.95
700	0.009	9	0.95
710	0.009	9	0.95
720	0.009	9	0.95
730	0.009	9	0.95
740	0.011	11	1.04
750	0.013	13	1.11
775	0.016	16	1.20
800	0.015	15	1.18
825	0.018	18	1.26
850	0.020	20	1.30
900	0.020	20	1.30

NICKEL DI-(3-ETHOXYSALICYLAL)-HEXAMETHYLENEDIIMINE
IN PYRIDINE

0.0001 M				0.001 M			
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.305	3050	3.48	430	6.620	620	2.79
330	0.312	3120	3.49	440	0.185	185	2.27
340	0.323	3230	3.51	450	0.085	85	1.93
350	0.379	3790	3.58	460	0.055	55	1.74
360	0.494	4940	3.69	470	0.037	37	1.57
370	0.615	6150	3.79	480	0.024	24	1.38
380	0.694	6940	3.84	490	0.013	13	1.11
390	0.700	7000	3.85	500	0.008	8	0.90
400	0.605	6050	3.78	510	0.005	5	0.70
410	0.427	4270	3.63	520	0.004	4	0.60
420	0.207	2070	3.32	530	0.005	5	0.70
425	0.124	1240	3.09	540	0.006	6	0.78
430	0.070	700	2.85	550	0.006	6	0.78
440	0.026	260	2.42	560	0.007	7	0.85
450	0.015	150	2.18	570	0.008	8	0.90
460	0.011	110	2.04	580	0.010	10	1.00

NICKEL DI-(3-ETHOXYSALICYLAL)-HEXAMETHYLENEDIIMINE IN PYRIDINE

0.001 M (cont.)

Wave Length	D	E	log E
590	0.009	9	0.95
600	0.009	9	0.95
610	0.010	10	0.90
620	0.008	8	0.85
630	0.007	7	0.78
640	0.006	6	0.60
650	0.004	4	0.60
660	0.004	4	0.60
670	0.002	2	0.30
680	0.001	1	0
690	0	0	-

NICKEL DI-(3-ETHOXYSALICYLAL)-HEPTAMETHYLENEDIIMINE

IN PYRIDINE

0.0001 M				0.001 M			
Wave Length	D	E	log E	Wave Length	D	E	log E
320	0.243	2431	3.39	450	0.816	816	2.91
330	0.209	2090	3.32	460	0.315	315	2.50
340	0.223	2230	3.35	470	0.145	145	2.16
350	0.302	3020	3.48	480	0.093	93	1.97
360	0.436	4360	3.64	490	0.072	72	1.86
370	0.619	6190	3.79	500	0.058	58	1.76
380	0.768	7680	3.89	510	0.050	50	1.70
390	0.825	8250	3.92	520	0.044	44	1.64
400	0.780	7800	3.89	530	0.041	41	1.61
410	0.658	6580	3.82	540	0.039	39	1.59
420	0.385	3850	3.59	550	0.040	40	1.60
430	0.300	3000	3.48	560	0.037	37	1.57
440	0.157	1570	3.20	570	0.036	36	1.56
450	0.067	670	2.83	580	0.033	33	1.52
460	0.027	270	2.43	590	0.029	29	1.46
470	0.014	140	2.15	600	0.025	25	1.40

NICKEL DI-(3-ETHOXYSALICYLAL)-HEPTAMETHYLENEDIIMINE

IN PYRIDINE

0.001 M (cont.)

Wave Length	D	E	log E
610.	0.022	22	1.34
620	0.018	18	1.26
630	0.016	16	1.20
640	0.013	13	1.11
650	0.011	11	1.04
660	0.009	9	0.95
670	0.008	8	0.90
680	0.007	7	0.85
690	0.006	6	0.78
700	0.005	5	0.70
710	0.005	5	0.70
720	0.005	5	0.70
740	0.005	5	0.70
770	0.009	9	0.95
800	0.011	11	1.04
830	0.016	16	1.20

NICKEL DI-(3-ETHOXYSALICYLAL)-NONAMETHYLENEDIIMINE

IN PYRIDINE

0.0001 M

Wave Length	D	E	Log E
320	0.362	3620	3.56
330	0.400	2000	3.60
340	0.393	3930	3.59
350	0.366	3660	3.56
360	0.371	3710	3.57
370	0.400	4000	3.60
380	0.425	4250	3.63
390	0.412	4120	3.62
400	0.350	3500	3.54
410	0.245	2450	3.39
420	0.120	1200	3.09
430	0.050	500	2.70
440	0.028	280	2.45

0.001 M

Wave Length	D	E	Log E
430	0.520	520	2.72
440	0.200	200	2.30
450	0.119	119	2.08
460	0.086	86	1.94
470	0.061	61	1.79
480	0.043	43	1.63

0.001 M

Wave Length	D	E	log E
490	0.027	27	1.43
500	0.019	19	1.28
510	0.011	11	1.04
520	0.006	6	0.78
530	0.003	3	0.48
540	0.002	2	0.30
550	0.004	4	0.60
560	0.005	5	0.70
570	0.007	7	0.85
580	0.008	8	0.90
590	0.009	9	0.95
600	0.007	9	0.85
610	0.009	9	0.90
620	0.009	9	0.95
630	0.009	9	0.95
640	0.008	8	0.90
650	0.007	7	0.85
660	0.007	7	0.85
670	0.005	5	0.70
680	0.005	5	0.70
690	0.005	5	0.70

NICKEL DI-(3-ETHOXYSALICYLAL)-NONAMETHYLENEDIIMINE IN PYRIDINE

0.001 M (cont.)

Wave Length	D	E	log E
700	0.005	5	0.70
710	0.004	4	0.60
720	0.003	3	0.48
730	0.003	3	0.48
740	0.002	2	0.30
750	0.003	3	0.48
760	0	0	0
775	0.002	2	0.30
800	0.002	2	0.30
810	0.002	2	0.30
820	0.003	3	0.48

NICKEL DI-(3-ETHOXYSALICYLAL)-DECAMETHYLENEDIIMINE IN PYRIDINE

0.0001 M				0.001 M			
Wave Length	D	E	log E	Wave Length	D	E	Log E
320	0.216	2160	3.34	430	0.568	568	2.75
330	0.246	2460	3.39	440	0.165	165	2.22
340	0.253	2530	3.40	450	0.088	88	1.95
350	0.238	2380	3.38	460	0.062	62	1.79
360	0.236	2370	3.38	470	0.047	47	1.42
370	0.255	2550	3.41	480	0.036	36	1.56
380	0.272	2720	3.44	490	0.026	26	1.42
385	0.268	2680	3.43	500	0.017	17	1.23
380	0.268	2680	3.43	510	0.011	11	1.04
400	0.225	2250	3.35	520	0.007	7	0.85
410	0.155	1550	3.19	530	0.005	5	0.70
420	0.075	750	2.88	540	0.005	5	0.70
430	0.027	270	2.43	550	0.005	5	0.70
440	0.015	150	2.18	560	0.006	6	0.78
				570	0.008	8	0.90
				580	0.009	9	0.95
				590	0.010	10	1.00
				600	0.011	11	1.04
				610	0.012	12	1.08
				620	0.010	10	1.00
				630	0.010	10	1.00
				640	0.008	8	0.90
				650	0.008	8	0.90

NICKEL DI-(3-ETHOXYSALICYLAL)-DECAMETHYLENEDIIMINE

IN PYRIDINE

0.001 M (cont.)

Wave Length	D	E	log E
660	0.007	7	0.85
670	0.006	6	0.78
680	0.005	5	0.70
690	0.005	5	0.70
700	0.004	4	0.60
710	0.004	4	0.60
720	0.001	1	0
730	0.001	1	0
740	0.001	1	0
750	0.001	1	0
760	0.001	1	0
770	0	0	-
780	0.002	2	0.30
790	0.003	3	0.48
800	0.003	3	0.48

DI-(SALICYLAL)-ETHYLENEDIIMINE IN PYRIDINE

0.0001 M				0.001 M			
Wave Length	D	E	log E	Wave Length	D	E	Log E
320	0.683	6830	3.83	360	0.425	425	2.63
330	0.558	5580	3.75	370	0.198	198	2.30
340	0.292	2920	3.47	380	0.134	134	2.13
350	0.122	1220	3.12				
360	0.068	680	2.83	390	0.109	109	2.04
370	0.053	530	2.72	400	0.100	100	2.00
380	0.044	440	2.64	410	0.093	93	1.97
				420	0.085	85	1.93
				430	0.072	72	1.86
				440	0.055	55	1.74
				450	0.036	36	1.56
				460	0.018	18	1.26
				470	0.008	8	0.90
				480	0.003	3	0.48
				490	0.001	1	0.
				thru			
				800	0.001	1	0

DI-(3-ETHOXYSALICYLAL)-ETHYLENEDIIMINE IN PYRIDINE

Wave Length	D	E	log E	Wave Length	D	E	Log E
		0.0001 M			0.01 M		
320	0.329	3290	3.52	480	0.452	45.2	1.66
330	0.422	4220	3.63	490	0.230	23.0	1.36
340	0.453	4530	3.66	500	0.100	10.0	1.00
350	0.404	4040	3.61	510	0.045	4.5	0.65
360	0.294	2940	3.47	520	0.022	2.2	0.34
370	0.187	1870	3.27	530	0.017	1.7	0.23
380	0.102	1020	3.01	540	0.015	1.5	0.18
390	0.060	600	2.78	550	0.013	1.3	0.11
400	0.038	380	2.58	560	0.014	1.4	0.15
410	0.024	240	2.38	570	0.010	1.0	0
		0.001 M					
370	0.980	980	2.99				
380	0.455	455	2.66				
390	0.267	267	2.43				
400	0.208	208	2.32				
410	0.193	193	2.29				
420	0.185	185	2.27				
430	0.174	174	2.24				
440	0.158	158	2.20				
450	0.135	135	2.13				
460	0.106	106	2.03				
470	0.075	75	1.88				
480	0.047	47	1.67				
490	0.024	24	1.38				

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